# MEMOIRS

OF THE

# COLLEGE OF SCIENCE

KYOTO IMPERIAL UNIVERSITY

VOL. I NO. 1.

OCTOBER 1914

KYOTO

# On the Beckmann Rearrangement. III.

By

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(Reprinted from Mem. Coll. Sci. Engin., VI.)

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An explanation for the mechanism of the Beckmann rearrangement has been brought forward by one of us and Todo in their recent article[1], based upon the assumptions that the primary cause of rearrangement consists in the dissociation of an acid residue from nitrogen in the oxime ester formed in reaction, and as its consequence an interchange of positions between a hydrocarbon radical linked to carbon and an acid residue attached to nitrogen may be effected, and that such a mobility of the acid residue may stand in a close connection with the strength of its negative character, since in the case of the acetyl oximes rearrangement is hardly brought about by heat alone when an acid such as hydrochloric acid is not present, while in the case of the benzenesulphonyl oximes rearrangement is spontaneously effected.

Now the presence of the acid residue must be a necessary condition of the Beckmann rearrangement; it is then assumed that the oximes would at first yield their esters, say by acid chlorides, and subsequently an acid residue and a hydrocarbon radical may exchange their positions, the dissociation primarily taking place in the case of the oxime esters containing the residue of strong acid without the aid of any reagent, sometimes by mere elevation of temperature, while in the case of the esters containing the residue of weak acid the tendency to dissociate may be accelerated by the aid of hydrochloric acid forming their hydrochlorides, or by its joint action with heat; as has been already pointed out[2]:

$$\begin{array}{l} C_6H_5.C.C_6H_5 \\ \quad\| \uparrow\downarrow \\ \quad N.OSO_2.C_6H_5 \end{array} \longrightarrow \begin{array}{l} C_6H_5.C.OSO_2.C_6H_5 \\ \quad\| \\ \quad N.C_6H_5 \end{array}$$

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1 Mem. Coll. Sci. Engin., Kyoto, **2**, 387 (1909–1910).

2 *Ibid.*, **2**, 394 (1909–1910).

$$\begin{array}{l} C_6H_5.C.C_6H_5 \\ \quad\| \uparrow \downarrow \\ HCl,N.OCO.CH_3 \end{array} \longrightarrow \begin{array}{l} C_6H_5.C.OCO.CH_3 \\ \quad\| \\ HCl,N.C_6H_5 \end{array}$$

Admitting the presence of the acid residue in the oxime as a necessary condition of rearrangement, the several facts relating to the decomposition of dihydroxamic acids may be regarded as giving a support to the authors' view.

Lossen and Rotermund[1] have shown that the neutral potassium salt of dibenzhydroxamic acid in its aqueous solution gives benzoic acid, carbon dioxide and diphenylurea on standing by itself or by heating:

$$2C_6H_5.C(OK):N.OCO.C_6H_5 + H_2O = 2C_6H_5.COOK + CO_2 + (C_6H_5.NH)_2CO.$$

Thiele and Pickard[2] have also pointed out that in the rearrangement of potassium salts of dihydroxamic acids the splitting up of a salt into an isocyanate and a potassium salt of the acid related to the acid residue linked to the nitrogen of the oxime group must be brought about at first:

$$R.C(OK):NOCOR' = R.N:C:O + KOCOR'$$

and then the formation of a symmetrical disubstituted urea would take place by the interaction of the isocyanate formed and water:

$$2R.N:C:O + H_2O = (RNH)_2CO + CO_2.$$

The free dihydroxamic acids also yield the analogous products of decomposition by heating at high temperature or by dry distillation.[3]

The authors have now to assert that in those cases of decomposition of dihydroxamic acids and their salts through the Beckmann rearrangement which is, we believe, wholly dependent upon the presence of acid residue, the interchange of positions between an acid residue and a hydrocarbon radical must occur, being preceeded by the dissoci-

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1 Lieb. Ann., **161**, 359 (1872); **175**, 257 (1875).

2 *Ibid.*, **309**, 189 (1899).

3 *Ibid.*, **175**, 311, 312 (1875); **309**, 189 (1899); Ber. D. chem, Ges., **27**, 1256 (1894).

ation of the former as the primary cause of rearrangement, and resulting in the formation of an acyl derivative of a substituted iminocarbonic acid as an intermediate product which would break up into an isocyanate and an acid or salt, and finally in the production of a disubstituted urea by the action of water upon the isocyanate; then, taking as an example the decomposition of dibenzhydroxamic acid and its potassium salt, the course of reaction should be represented as follows[1]:

$$\begin{matrix} C_6H_5.C.OH(K) \\ \| \\ C_6H_5.COO.N \end{matrix} \longrightarrow \begin{matrix} C_6H_5.COO.C.OH(K) \\ \| \\ C_6H_5.N \end{matrix} \longrightarrow \begin{matrix} C_6H_5.COOH(K) \\ \hline\hline \\ C_6H_5.N{:}C{:}O \end{matrix}$$

$$\begin{matrix} C_6H_5.N{:}C{:}O \\ C_6H_5.N{:}C{:}O \end{matrix} + H_2O = \begin{matrix} C_6H_5.NH \\ C_6H_5.NH \end{matrix}\!\!>\!CO + CO_2.$$

Thus, in the rearrangement of several other dihydroxamic acids and their potassium salts[2] which behave similarly as dibenzhydroxamic acid and its potassium salt, giving the analogous decomposition products under an analogous condition, the mechanism of reaction should be analogous.

The authors repeated Lossen and Rotermund's[3] experiment, by distilling an aqueous solution of the neutral potassium salt of dibenzhydroxamic acid, and also observed the production of aniline which must be due to the formation of diphenylurea, caused by the Beckmann rearrangement owing to the presence of the benzoic acid residue. We could, however, not find even a trace of aniline from the potassium salt of benzhydroxamic acid and from ethylsynbenzhydroximic acid[4]:

$$\begin{matrix} C_6H_5.C.OK \\ \| \\ HO\text{-}N \end{matrix} \quad \text{and} \quad \begin{matrix} C_6H_5.C.OC_2H_5 \\ \| \\ HO\text{-}N \end{matrix}$$

by distilling an aqueous solution of the former, and by heating the latter above its melting point for several hours and then distilling the product with aqueous alkali. This makes it evident that the Beckmann rearrangement would not take place in the salt and ester of benzhydrox-

1 Such a scheme of reaction is seen in Meyer and Jacobson's Lehrbuch d. org. Chemie, 1st ed., II, 560, but nothing is said about the essence which may lead to rearrangement.

2 Lieb. Ann., **175**, 311, 312 (1875); **309**, 189 (1899); Amer. Chem. J., **48**, 1 (1912).

3 *Ibid.*, **161**, 359 (1872); **175**, 257 (1875).

4 Ber. D. chem. Ges., **25**, 37 (1892).

amic acid, for the necessary acid residue is lacking in each. Also, the facts already observed by Hantzsch[1] appear to give a further support to the authors' view. He has shown that by gently warming the potassium carbonate solution of acetylbenzhydroxamic acid, $C_6H_5.C(OK):N.OCO.CH_3$, diphenylurea abundantly separates out, while with the potassium carbonate solution of free benzhydroxamic acid, $C_6H_5C(OK):N.OH$, no such a decomposition takes place even by boiling. The authors, now, dare to explain by ascribing such a difference of the behaviours of two compounds to the presence and absence of the acetic acid residue in acetylbenzhydroxamic and benzhydroxamic acids respectively.

It is already known that ethyl dibenzhydroxamate of the syn form (i.e., ethylsynbenzhydroximic acid benzoyl ester)[2] is decomposed into benzonitrile, benzoic acid and acetaldehyde by heating above its melting point; and the reaction has been pointed out as follows[3];

$$\begin{matrix} C_6H_5.C.OC_2H_5 \\ \| \\ C_6H_5.COO.N \end{matrix} \longrightarrow \begin{matrix} C_6H_5.COO.C.OC_2H_5 \\ \| \\ C_6H_5.N \end{matrix}$$

$$\longrightarrow C_6H_5.COOH + C_2H_4O + C_6H_5.NC.$$

So, we declare that in the case of ethylsynbenzhydroximic acid benzoyl ester, the Beckmann rearrangement should take place, for it may be regarded as the ethylbenzhydroximic acid derivative containing the benzoic acid residue linked to nitrogen in the syn form.

In order to get a further confirmation for the authors' view, two isomeric acetyl esters of ethylbenzhydroximic acid[4]:

$$\begin{matrix} C_6H_5.C.OC_2H_5 \\ \| \\ CH_3.COO.N \end{matrix} \quad \text{and} \quad \begin{matrix} C_6H_5.C.OC_2H_5 \\ \| \\ N.OCO.CH_3 \end{matrix}$$

were heated above their melting points for some hours, and the product from each ester was subjected to steam distillation in alkaline solution, as in the experiment of ethylbenzhydroximic acid. By such

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1 Ber. D. chem. Ges., **27**, 1257 (1894).

2 Lieb. Ann., **205**, 279 (1880); Ber. D. chem. Ges., **25**, 44 (1892).

3 Meyer and Jacobson's Lehrbuch d. org. Chemie, 1st ed., II, 561.

4 Ber. D. chem. Ges., **25**, 40–41 (1892).

a treatment a small quantity of aniline was found to be formed from the syn acetyl ester, but not a trace from the anti ester; so the production of aniline may be due to the decomposition of urethane somewhat formed from the syn ester as the result of the Beckmann rearrangement by heat, the reaction being assumed to be:

$$\begin{matrix} C_6H_5.C.OC_2H_5 \\ \| \\ CH_3.COO.N \end{matrix} \xrightarrow{\text{Heat}} \begin{matrix} CH_3.COO.C.OC_2H_5 \\ \| \\ C_6H_5.N \end{matrix} \xrightarrow{H_2O} \begin{matrix} O:C.O.C_2H_5 \\ | \\ C_6H_5.NH \end{matrix}$$

Such a course of reaction as we assume, and that for the production of phenylurethane from ethylsynbenzhydroximic acid by phosphorus pentachloride and water, which has been pointed out by Werner[1], should be no doubt same in essence.

Moreover, each of two isomeric acetyl esters was heated in a sealed tube, dissolved in chloroform saturated with hydrochloric acid, at the temperature of 100–102° for twelve hours. The product from the syn acetyl ester was observed to contain phenylurethane and acetyl phenylurethane, but that from the anti ester not at all. The authors, then, admit it as correct that in the case of the syn acetyl ester the Beckmann rearrangement is accelerated by the aid of hydrochloric acid, just as has been shown in the rearrangement of the acetyl ester of diphenylketoxime[2], thus being represented as follows:

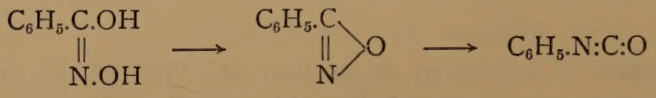
$$\begin{matrix} C_6H_5.C.OC_2H_5 \\ \| \\ CH_3.COO.N,HCl \end{matrix} \longrightarrow \begin{matrix} CH_3.COO.C.OC_2H_5 \\ \| \\ C_6H_5.N,HCl \end{matrix} \longrightarrow$$

$$\begin{matrix} O:C.OC_2H_5 \\ | \\ C_6H_5.NH \end{matrix} + CH_3.COCl \longrightarrow \begin{matrix} O:C.OC_2H_5 \\ | \\ C_6H_5.N.COCH_3 \end{matrix}$$

Lossen[3] has announced that benzhydroxamic acid and its barium salt decompose into aniline and carbon dioxide by dry distillation. According to his statement, rearrangement actually takes place in

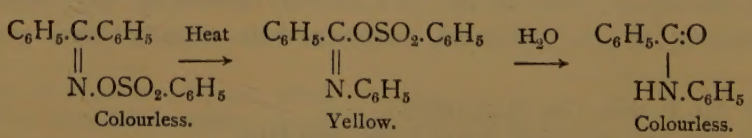
1 Ber. D. chem. Ges., **25**, 39 (1892).
2 Mem. Coll. Sci. Engin., Kyoto, **2**, 394 (1909-1910).
3 Lieb. Ann., **175**, 320, 323 (1875).

benzhydroxamic acid and its salt, although they do not contain the negative acid residue; in this case, therefore, the decomposition can not be accounted for as the result of the Beckmann rearrangement of the usual type, as we assume, so it may be founded upon some other scheme of reaction. The authors then put forward an explanation by applying Hantzsch's view[1] on the rearrangement of benzhydroxamic acid, that is to say, that benzhydroxamic acid forms an anhydride which intramolecularly undergoes rearrangement:



Now, it has become evident that rearrangement does not take place in an aqueous solution of the salt of benzhydroxamic acid, as has already been stated, because the formation of an anhydride is not possible on account of the presence of water. Nevertheless, in an aqueous solution of the salt of hydroxamic acid acyl ester (dihydroxamic acid), in fact rearrangement takes place, as is indicated by the production of disubstituted urea as has been stated, although the formation of hydroxamic acid or its salt is possible by hydrolysis, but their rearrangement should not take place as their dehydration can not be effected in presence of water; in such a case, therefore, the migration of a negative acid residue must be brought about as the primary cause of rearrangement.

Recently an interesting observation was made by one of us (M.K.), Nakaseko and Matsunami in our laboratory with regard to the rearrangement of benzenesulphonyl ester of diphenylketoxime, viz., that the ester prepared from the sodium salt of diphenylketoxime by the action of benzenesulphonyl chloride at a low temperature, which is a colourless crystalline substance, changes to a yellow coloured compound gradually on standing by itself, but instantaneously with explosive violence accompanied by a hissing sound by heating; the yellow compound being unstable, changes readily to benzanilide by treating with water. The course of reaction shall be represented by the following scheme:




[1] Ber. D. chem. Ges., **27**, 1255 (1894).

in which the formula of the intermediate product points out the presence of a characteristic chromophoric group, $>C{:}N.C_6H_5$.[1]

Also, Hermann Weg[2] has shown that benzensulphonyl ester of acetoxime, $(CH_3)_2C{:}N.OSO_2.C_6H_5$, decomposes explosively with a hissing noise by heating, but nothing is said about the production of a substituted acid amide. Yura, however, found as the result of an experiment suggested by one of us (M.K.) that the principal decomposition product consists of a methylamine-producing compound which may be regarded as methylacetamide, as it yields methylamine by treating with alkali; thus the reaction shall be represented as follows:

$$\begin{matrix} CH_3.C.CH_3 \\ \| \\ N.OSO_2.C_6H_5 \end{matrix} \xrightarrow{\text{Heat}} \begin{matrix} CH_3.C.OSO_2.C_6H_5 \\ \| \\ N.CH_3 \end{matrix} \xrightarrow{H_2O} \begin{matrix} CH_3.C{:}O \\ | \\ CH_3.NH \end{matrix}$$

He further experimented with the benzoyl and acetyl esters of acetoxime, and observed, likewise, the production of methylamine from the decomposition product, although not so much as in the case of benzenesulphonyl ester.

Jones[3] has recently mentioned in his article that the potassium salt of the benzoyl ester of phenylacethydroxamic acid, $C_6H_5.CH_2C(OK){:}N.OCO.C_6H_5$, dried upon a porous support, suddenly decomposes in the course of a few minutes, accompanied by a hissing sound and a dense cloud of benzylisocyanate, and also that in a similar manner, certain other salts of hydroxamic acids, when heated to a temperature considerably above room temperature, decompose explosively. Thiele and Pickard[4] already noticed that acetyl and benzoyl esters of hydroxamic acid yield potassium salts which explodes by heating. So, the authors believe that such a decomposition is due to the spontaneous rearrangement analogous to that of the ketoxime esters as above stated.

Now, such an explosion with a hissing sound, which occurs suddenly in the decomposition of the different compounds of the oxime type may be regarded as a particular phenomenon accompanying the spontaneous Beckmann rearrangement, viz., the self-migration of an acid residue and a hydrocarbon radical.

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1 Mem. Coll. Sci. Engin., Kyoto. **2**, 356 (1909–1910).
2 Ber. D. chem. Ges., **24**, 3537 (1891).
3 Amer. Chem. J., **48**, 8 (1912).
4 Liebig Ann. **309**, 190 (1899).

The investigation relating to the rearrangement of benzenesulphonyl and other acyl esters of different ketoximes is now in progress; the details of the result will be communicated in a near future.

## EXPERIMENTAL.

### 1. *Potassium Dibenzhydroxamate,*

$C_6H_5.C(OK):N.OCO.C_6H_5$.

Five grams of dibenzhydroxamic acid prepared according to the method by Lossen[1], was suspended in water, and a solution of potassium hydroxide was carefully added until it dissolves, and then the solution was subjected to distillation by passing a current of steam. Adding a drop of a solution of bleaching powder to a small portion of the distillate, there was observed the characteristic colour-reaction of aniline. The principal portion of the distillate was extracted with ether, and the liquid substance left on evaporation of ether was confirmed to be aniline by changing it to the double salt of its hydrochloride with platinum chloride.

The similar experiment was conducted by usiug an aqueous solution of the neutral potassium salt of dibenzhydroxamic acid, prepared as usual, by treating the acid with alcoholic potash. The result was found to be same as above described.

### 2. *Potassium Benzhydroxamate,* $C_6H_5.C(OK):N.OH$.

The experiment exactly similar to that above stated was performed with the potassium salt of benzhydroxamic acid from the acid prepared according to the statement given by Lossen[2], but not a trace of aniline was found to be formed, not giving the characteristic delicate colour-reaction of aniline.

### 3. *Ethylbenzhydroximic acids,* $C_6H_5.C(OC_2H_5):N.OH$.

Each of both geometrical isomers of ethylbenzhydroximic acid (the syn ester melts at 53° and the anti at 67°)[3] was heated at the tem-

[1] Lieb. Ann., **161**, 347 (1872).

[2] *Ibid.*

[3] Ber. D. chem. Ges., **17**, 1587 (1884); **25**, 37-39 (1892); Lieb. Ann., **205**, 279 (1880.)

perature of 70–80° for twelve hours over a water bath. The product from each was subjected to steam distillation in an alkaline solution, but the distillate gave no colour-reaction of aniline at all. Hence, it is concluded that the Beckmann rearrangement would not take place in the potassium salt and both esters of benzhydroxamic acid.

### 4. *Ethylbenzhydroximic Acetates,*

$C_6H_4.C(OC_2H_5):N.OCO.CH_3$

Syn and anti acetates of ethylbenzhydroximic acid prepared according to Werner's description[1] melt at 38–39° and 57° respectively.

Three grams of the syn acetate were heated at the temperature of 67–70° for twelve hours, and the product was subjected to steam distillation in an alkaline solution. The production of a small quantity of aniline was confirmed in the distillate by the colour-reaction with a bleaching powder solution.

### 5. *Action of Hydrochloric Acid upon Ethylbenzhydroximic Acetates.*

Three grams of ethylsynbenzhydroximic acetate dissolved in 30 c.c. of chloroform saturated with hydrochloric acid were heated in a sealed tube at 100-102° for twelve hours. When the tube was opened, the escapement of ethyl chloride was noticed; the contents of the tube were poured into a glass vessel where chloroform and hydrochloric acid were driven out by evaporation, a reddish brown liqnid being left as a residue. From this liquid, phenylurethane and acetyl benzhydroxamic acid were isolated. In order to conduct the separation of those compounds, the reaction products were first treated with ether and then with benzene, as phenylurethane and acetyl phenylurethane are soluble in ether while acetyl benzhydroxamic acid not in ether but in benzene and water. Each of those substances was identified by its melting point and other characteristic behaviours.

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1 Ber. D. chem. Ges., **25**, 40–41 (1892).

# Meteoreinfälle als Ursache des vermuteten Zurückhaltens der obersten Atmosphäre.

VON

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(Abgedruckt nach Mem. Coll. Sci. Engin., VI.)

## I.

Es scheinen nach Wegener[1] in den grossen Höhen der Erdatmosphäre immer dauernde Ostwinde mit bedeutender Geschwindigkei tzu herrschen. Dies begründet er durch die folgenden Beobachtungstatsachen :—

(i) dass die Pilotballonaufstiege über Uccle im Jahre 1907 OSO-Wind in den Höhen von 20 bis 26 km gezeigt haben;

(ii) dass die Bewegung der Rauchmassen des Krakatoa-Ausbruchs Ostwind in den grossen Höhen mit einer mittleren Geschwindigkeit zwischen 35 und 45 Meter pro Sek. gezeigt hat;

(iii) dass die Ausbreitung der leuchtenden Nachtwolken, 1889–1891, Ostwind mit einer Geschwindigkeit von 100 Meter pro Sek. in der Höhe von 80 km gezeigt. hat,

und daraus schliesst er dass man hier mit dem Zurückhalten der obersten Atmosphäre zu tun habe. Die rückwärtige Bewegung beträgt in der Höhe von 100 km etwa ein Drittel der Geschwindigkeit der Erdoberfläche.

Diese Erscheinung, das Zurückhalten der obersten Erdatmosphäre, ist sehr bemerkenswert, um so mehr, als es in diesen grossen Höhen keine Vertikalströmung zu erwarten wäre, weshalb es keine Folge von den thermodynamischen Erscheinungen an der Erdoberfläche sein könnte. Uns lehrt eine theoretische Betrachtung[2] des Gleichgewichtes der Planetenatmosphäre, dass die Erdatmosphäre bis zur Höhe von sechsmal

1 Met. Zs., 28, 271 (1911).

2 Tisserand, Méc. Cél., IV, 233.

Erdradien die ganze Rotation des Kerns mitmachen wird. Auch eine gastheoretische Ueberlegung[1] äusserst verdünnter Atmosphäre gibt uns keinen Anhaltepunkt zu Gunsten des Zurückhaltens. Die beobachtete Erscheinung fordert demnach irgend welche positive Ursache für die Erklarüng derselben. Es wird im folgenden versucht, die Meteoreinfälle als solche zu betrachten, und dann wird es gezeigt, dass man hier in dieser Erscheinung die beste Methode findet, um die totale Menge der Meteormassen, die die Erde jährlich aufnimmt, am sichersten zu schätzen.

## II.

Was nun die Meteoreinfälle in unsere Atmosphäre betrifft können wir die beobachteten Tatsachen[2] etwa folgendermassen auffassen;—

(i) Die Sternschnuppen sind uns sichtbar in den Höhen zwischen 90–150 km. Die tägliche Zahl über der ganzen Erde beträgt etwa $2 \times 10^7$. Die mittlere Lichtstärke gleicht derjenigen eines Sterns $3^{ter}$ Grösse, und die mittlere Zeitdauer des Leuchtens ist etwas kleiner als eine Sekunde.

(ii) Die viel kleineren Sternschnuppen sind nur teleskopisch sichtbar, und die mittlere Höhe des Leuchtens ist natürlich viel grösser, so etwa über 200 km. Die Anzahl solcher teleskopischen Sternschnuppen schätzt man etwa 100–mal so gross wie die visuellen. Die mittlere Lichtstärke gleicht etwa derjenigen eines Sterns $9^{ter}$ Grösse.

(iii) Die grösseren, die man als Feuerkugeln beobachtet, kommen viel näher zur Erde, so etwa bis zur Höhe von 50 km oder noch weniger. Nach der Lichtstärke zu schätzen, müssen sie im Durchschnitt etwa 1000-mal grösser sein als die mittlere visuelle Sternschnuppe,

(iv) Die noch grösseren endlich fallen zur Erde und werden uns wahrnehmbar als Meteoriten. Es sind welche die mehrere Tonnen wiegen. Die Anzahl schätzt man als etwa 1000 pro Jahr.

(v) Aus dem Zahlenverhältnis der visuellen Sternschnuppen in Morgen- und Abendstunden konnte man schliessen, dass sie sich meistenteils in kleinen elliptischen Bahnen um die Sonne bewegt haben[3]. Für mehrere, die zu den Klassen (iii) und (iv) gehören, konnte man

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[1] C. G. Darwin, Phil. Mag., [6] **23**, 664 (1912).

[2] Herz, Kometen u. Meteore in Valentiner's Handwörterbuch; Newton, Meteor in Encyc. Brit, 9te aufl., XVI.

[3] Herz, Kometen u. Meteore in Valentiner's Handwörterbueh, II, 169.

sogar ihre Bahnen näher bestimmen[1] und hat dabei diese Tatsache bestätigt gefunden.

Diesen Zusammensetzungen zufolge machen wir die folgenden Annahmen als die erste Annäherung für den vorliegenden Zweck:—

(A) Die Gesamtmeteormassen kommen nur bis zur Höhe von h km; ihre Bewegung wird dort gehemmt.

(B) Das resultierende Flächenmoment aller einfallenden Meteormassen um den Erdschwerpunkt ist gleich Null.

Solange wir die Rotation der obersten Atmosphärenschichten als ganzes betrachten, brauchen wir also einfach den Flächensatz um die Erdachse niederzuschreiben:—

$$\int \mu \times (1-f)\, v \times \rho dS = \int \frac{fv}{h} \times \eta \times \rho dS,$$

wo

$\mu$ = Meteoreinfall pro Sek. pro Flächeneinheit,

$v$ = Lineare Geschwindigkeit der Erdoberfläche,

$fv$ = Ostwind in der Höhe h,

$\eta$ = mittlerer Viskositäts-koeffizient der atmosphärischen Luft,

$dS$ = Flächenelement,

$\rho$ = Abstand von $dS$ von der Rotationsachse.

Wenn wir weiter annehmen, dass $m$, $f$ und $h$ in allen Gegenden konstant sind, oder vielmehr wollen wir sagen, wenn wir nur die mittleren Werte dieser Grössen betrachten, so haben wir

$$\mu = \frac{f}{1-f} \times \frac{\eta}{h},$$

und

$$M = \mu \times 4\pi R^2 = \frac{f}{1-f} \times \frac{\eta}{h} \times 4\pi R^2.$$

Setzen wir numerisch

$$h = 10^7\, cm$$

$$f = \frac{1}{3}$$

1 Denning, Meteor in Encyc. Brit., 10te Aufl., XXX., 661.

$$\eta = 8 \times 10^{-5} \frac{gr}{cm \,.\, sek}$$ [1]

$$R = 6{\cdot}4 \times 10^{8}\, cm,$$

so erhalten wir

$$\mu = 4 \times 10^{-12} \frac{gr}{cm^2 .\, sek},$$

$$M = 2 \times 10^{7} \frac{gr}{sek}.$$

Für den Wert von $\eta$ haben wir keine sicheren Daten; der Grössenordnung nach aber wird es wohl nicht viel anderes geben. Wir sehen also, dass das Einfallen von Meteormassen in einer Menge von etwa 20 Tonnen pro Sekunde genügen wird, um die beobachtete Erscheinung des Zurückhaltens der obersten Atmosphäre zu erklären.

Es muss hier auch bemerkt werden, dass bei der vorliegenden Rechnung stillschweigend angenommen ist, dass

(C) die oberste Atmosphäre kein Leiter der Electrizität ist. Wenn wir aber annehmen sollten, wie es die wirkliche Tatsache zu sein scheint, dass

(C′) die oberste Atmosphäre immer dauernde Ionisation erleidet, und deshalb etwaige Leitfähigkeit für Elektrizität hat,

dann stellt sich die Sache etwas anders heraus. Die Induktionswirkung des Erdmagnetismus wird elektrische Ströme in der leitenden Atmosphäre hervorrufen in der Richtung, wo die gegenseitige Wirkung gerade der Verschiebung des leitenden Körpers entgegenwirkt. Wir müssten also diese Gegenwirkung in Rechnung bringen, und die ausgerechnete Meteormasse würde dementsprechend um so grösser herauskommen. Weil aber diese Induktionswirkung eine wichtige Rolle spielen wird in der Theorie des Erdmagnetismus und der sekularen Änderung desselben, so werde ich lieber diese Erscheinung in einem anderen Aufsatze betrachten und einer eingehenden Untersuchung unterwerfen. Hier sei es nur so viel bemerkt, dass es sehr wohl möglich ist, dass der Wert von $M$ noch etwa hundertmal grösser herauskommen wird.

Dieser Betrag von Meteormassen ist bedeutend grösser als derjenige, den man in gewöhnlichen Lehrbüchern u.s.w. findet. Ich werde

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[1] Uber äussert verdünnten Stickstoff in niedriger Temperatur; sieh z.B. Winkelmann's Handbuch der Physik, I., 1407.

also im folgenden erst sehen, wie die Meteormassen bisher abgeschätzt worden sind.

## III.

Die Masse einzelner Meteoren oder die totale Menge der Meteormassen, die die Erde jährlich aufnimmt, abzuschätzen, hat man bisher in verschiedener Weise versucht, scheint aber immerhin auf keinem sicheren Grunde gestanden zu haben.

(1) Die ältere[1] und auch viel besprochene ist die Abschätzung der einzelnen Masse durch die Menge der ausgestrahlten Lichtenergie. Es sei für einen Meteor

$L$ = Lichtintensität,

$\tau$ = Zeitdauer des Leuchtens.

Wenn man die Leuchtkraft im Zustand des Meteorleuchtens $= F$ candle pro watt ansetzt, so ist die

$$\text{ausgestrahlte Energie} = \frac{L \times \tau}{F}.$$

Indem man nun dies gleich der ganzen verlorenen kinetischen Energie setzt, so erhält man

$$\frac{1}{2} mv^2 = \frac{L \times \tau}{F},$$

$$\therefore m = \frac{2.L.\tau}{F.v^2}.$$

Durch Einsetzen von passenden numerischen Werten für $L, \tau, F$ und $v$, bekommt man für $m$ eine winzige Grösse, einen kleinen Bruchteil von Gramm. Es ist aber ganz klar, dass der grösste Teil der anfänglichen kinetischen Energie unterwegs verbraucht und die Ausstrahlung nur ein kleiner Teil derselben ist. Es kann wohl ein Tausendstel sein, oder auch wohl ein Millionstel. Es ist unmöglich, in dieser Weise zu irgend einem Schluss gelangen zu können.

(2) Etwas sichere Bahn ist neulich von Pickering eingeschlagen[2]. Wenn die Flächenhellikeit des leuchtenden Meteors

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1 Young, General Astronomy.

2 Astroph. J., **29.** 378 (1909); **31,** 88 (1910).

$$= H \frac{candle}{mm^2}$$

angesetzt ist, so bekommt man

$$\text{die leuchtende Fläche} = \frac{L}{H}\, mm^2,$$

und folglich eine Dimension etwa von der Grösse

$$\sqrt{\frac{L}{H}} \text{ mm.}$$

(a) Pickering setzt

$H$ = die Flächenhelligkeit eines offenen Bogenlichtes in horizontaler Richtung

= 250 candle pro cm$^2$,

$$L = \left(\frac{150}{2.5}\right)^2 \times \frac{3 \times 250}{40} = 6{\cdot}8 \times 10^4 \text{ candle},$$

und so bekommt er

$$\sqrt{\frac{L}{H}} = 15-18 \text{ cm},$$

$$\therefore \rho \times \frac{\pi}{6} \times \left(\frac{4}{\pi} \times \frac{L}{H}\right)^{\frac{3}{2}} = \text{ca } 26 \text{ kg},$$

wenn man $\rho = 8$ setzt.

(b) Fabry setzt[1]

H = die Flächenhelligkeit des Kraters eines Bogenlichtes

= 200 candle pro mm$^2$,

$L$ = 4500 candle,

und so bekommt er

$$\frac{L}{H} = 23 \text{ mm}^2,$$

$$\rho \times \frac{\pi}{6}\left(\frac{4}{\pi} \times \frac{L}{H}\right)^{\frac{3}{2}} = \text{ca } 0{\cdot}3 \text{ gr},$$

ndem er $\rho = 4$ annimmt,

1 Astroph. J., **30**, 318 (1909).

(c) Wir haben aber nach Nernst[1] für die Flächenhelligkeit eines schwarzen Körpers in verschiedenen Temperaturen.

| $T_{abs}$ | $H \frac{\text{Candle}}{mm^2}$ | $T_{abs}$ | $H \frac{\text{Candle}}{mm^2}$ |
|---|---|---|---|
| 1524° | 0·2 | 2357 | 80 |
| 1685 | 1 | 2446 | 120 |
| 1764 | 2 | 2510 | 160 |
| 1982 | 10 | 2571 | 200 |
| 2092 | 20 | 2680 | 300 |
| 2217 | 40 | 2763° | 400 |

Wenn wir noch das Strahlungsvermögen der Meteorfläche etwa $=0{\cdot}5$ setzen, so sehen wir, dass die Annahme von Pickering einer Temperatur von $T=1890°$, und diejenige von Fabry einer Temperatur von $T=2763°$ entspricht. Wenn wir aber die Oberflächentemperatur des leuchtenden Meteors, etwa dem Schmelzpunkt des Eisens entsprechend, $=1764°$ abs. annehmen, und wieder das Strahlungsvermögen $=0{\cdot}5$ setzen, so haben wir $H=1$ candle pro $mm^2$, und dies gibt mit dem Pickering'schen Wert von $L$

$$\sqrt{\frac{L}{H}} = 26 \text{ cm},$$

$$\rho \times \frac{\pi}{6} \times \left(\frac{4}{\pi} \times \frac{L}{H}\right)^{\frac{3}{2}} = \text{ca } 100 \text{ kg},$$

wenn man $\rho=8$ setzt. Hundert Kilogramm pro Stück geben mit der täglichen Anzahl von $2 \times 10^7$,

$$M = 2{\cdot}3 \times 10^7 \frac{\text{gr}}{\text{sek}},$$

gerade dieselbe Grössenordnung wie der ausgerechnete Wert in II. Das Leuchten von Meteoren ist aber sicherlich keine reine Temperaturstrahlung, so dass der richtige Wert von H nicht leicht zu finden ist. Die Methode bleibt folglich in so fern fehlerhaft.

(3) Eine originelle Idee rührt von Humphreys[2] her. Er legt Yntema's Beobachtung von „Earth-light", d.h. von der Helligkeit des

1 Nernst; Physik. Zs., **7**, 380 (1906).

2 Astroph. J., **35**, 271, (1912).

sternleeren Himmelsgrundes zu Grunde. Die Zunahme dieser Helligkeit mit der Zenitdistanz und die zeitliche Veränderlichkeit wollte er durch die Annahme erklären, dass sie nicht kosmischen Ursprungs, sondern ein Aggregat von teleskopischen Sternschnuppen in unzählbarer Menge ist. Aus Yntema's Daten, dass diese Helligkeit etwa gleich ist einem Zehntel des Lichtes aus einem Stern 1$^{ster}$ Grösse pro Quadratgrad, rechnet er aus, dass sie $= 2 \times 10^{-4}$ m.c., und ferner, weil die Beleuchtung einer Fläche durch normales Sonnenlicht $= 10^5$ m.c. ist, so bekommt er

$$\text{die Helligkeit von "Earth-light"} = \frac{1}{5 \times 10^8} \times \text{Sonnenbeleuchtung.}$$

Nun macht er weitere Annahmen:

(i) dass die Verteilung der totalen ausgestrahlten Energie zwischen Licht und Wärme als gleichartig anzusehen ist für Meteor- und Sonnenlicht,

(ii) dass die totale kinetische Energie eines Meteors gänzlich als Strahlungsenergie verbraucht wird.

Er bekommt also, indem er die Solarkonstante $= 1.92$ setzt, die Gleichung

$$\frac{2}{5 \times 10^8} \times 1.92 \times 4\pi R^2 \frac{\text{calorie}}{\text{min.}} = 2{\cdot}7 \times 10^{15} \frac{\text{erg}}{\text{sec}} = \frac{1}{2} Mv^2.$$

Er setzt dann $v = 42 \frac{\text{km}}{\text{sec}}$,

und so bekommt er schliesslich

$$M = 3 \frac{\text{kg}}{\text{sec}}.$$

Wir sehen, dass die Annahme (ii) nicht richtig ist; die Methode (3) hat dieselbe Fehlerquelle wie die Methode (1). Ueberdies trifft die Annahme, dass das "Earth-light" ganz von telescopischen Sternschnuppen herrührt, auch nicht zu. Man müsste eigentlich zuerst die ganze Lichtmenge von teleskopischen Sternen in Rechnung bringen, was keineswegs zu vernachlässigen ist. Wenn man z.B. Lord Kelvin'sche[1] theoretische Abschätzung umrechnet, so bekommt man für die letztere gerade dieselbe Grössenordnung wie die totale Helligkeit von "Earth-light."

[1] Phil. Mag. [6], 2, 161, (1901).

Soweit sehen wir also, dass alle diese Methoden, die auf irdischen Erscheinungen beruhen, nicht ausreichen, um die Meteormassen zu bestimmen. Unser Wert von 20 Tonnen pro Sekunde und mehr steht einzig und sondergleichen da. Andererseits aber haben wir aus astronomischen Quellen noch zwei Abschätzungen, und zwar solche, die noch über hundertmal grössere Werte angeben.

(4) Die unaufgeklärte sekulare Beschleunigung der Mondbewegung im Betrag von 5″ in einem Jahrhundert versucht v. Oppolzer[1] durch Meteoreinfall zu erklären. Er findet, dass etwa $2 \times 10^8$ Tonnen pro Tag dazu nötig sein werden. Dieser Betrag ist 100 mal so gross als unser Wert in II. See[2] hat neulich v. Oppolzer'sche Rechnung korrigiert, indem er einerseits die Flutreibung in Rechnung bringt, und andererseits annimmt, dass etwa $\frac{1}{3}$ sämtlicher Meteore von einem Ring um die Erde herstammt. Diese Annahme; „That one third of all our meteoric dust should come from the vortex about the earth is highly probable" ruht aber auf keinen Beobachtungsdaten. Im Gegenteil steht das Vorhandensein der Ostwinde in höheren Schichten solcher Annahme direkt entgegen.

(5) Die Unregelmässigkeiten in der Bewegung der inneren Planeten versucht v. Seeliger[3] durch die Verteilung der Meteormassen im interplanetarischen Raume zu erklären. Er findet daraus, dass die Massendichte in der Gegend der Erdbahn = etwa 4 gr pro Quadratkilometer sein wird. Wenn wir vorläufig diese Masse als ruhend annehmen, so würde diese Meteoreinfall in Betrag von

$$1{\cdot}4 \times 10^9 \frac{\text{gr}}{\text{sec}}$$

verursachen, etwa siebzigmal so gross als unser Wert in II. Wir haben gegen Schluss der Sektion II darauf aufmerksam gemacht, dass wegen der elektromagnetischen Induction unser Wert von 20 Tonnen pro Sekunde noch mit einem Vergrösserungsfaktor multipliciert werden muss. Es ist sehr wahrscheinlich, dass der so vergrösserte Wert mit den Angaben von (4) und (5) gut harmoniren wird, wenn man die letzteren erst durch nähere Untersuchung korrigiert,

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1 Astr. Nachr. 2573 (1884); See—Evolution of the Stellar Systems, II. 299.

2 Evolution of the Stellar Systems, II., 318.

3 Münchener SitzBer., **36**, 620 (1906).

## IV.

Das Resultat der vorhergehenden Untersuchung ist nichts anders als die direkte Verbindung der zwei Tatsachen mit einander:

1. Das Zurückhalten der obersten Erdatmosphäre,
2. Meteoreinfall in grossen Mengen, d.h. $2 \times 10^7 \times k \frac{gr}{sec}$, wo k einen Vergrösserungsfaktor bedeutet.

Die eine ist die notwendige Folge der anderen. Die zwei Tatsachen, die im einzelnen betrachtet leider nicht sicher orientiert sind, bekommen dadurch stärkere gegenseitige Stütze.

Die erstere Tatsache spielt eine wichtige Rolle in der Theorie des Erdmagnetismus. Die zweite hat die bisherige niedrige Abschätzung der Meteormassen stark erhöht und wird dadurch die Bedeutung der Meteormassen im interplanetarischen Raume bei weitem vergrössern.

# Gleichzeitiges Entwickeln und Fixieren der Bromsilbergelatineplatten.

Von

**Chiri Otsuki und Takashi Sudzuki.**

(Abgedruckt nach Mem. Coll. Sci. Engin., VI.)

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Die heute in der Praxis des photographischen Negativ-Verfahrens ausschliesslich geübten Manupulationen, wonach die belichteten Platten erst entwickelt und dann fixiert werden müssen, werden von vielen Seiten als ziemlich umständlich betrachtet. Könnten diese beiden Operationen in eine vereinigt werden, würde es einerseits in bezug auf die Raumersparnis in der Dunkelkammer, andrerseits auf die Behandlung der Platten eine grosse Vereinfachung sein.

V. Crémier[1] und in neuerer Zeit J. Gaedicke[2] haben versucht, durch den Zusatz des Fixiernatrons zum Entwickler eine solche Flüssigkeit welche die Entwicklung und die Fixierung der Trockenplatten in einmaliger Operation durchführen lasse, herzustellen. Obgleich die von Crémier empfohlene Vorschrift;

| | |
|---|---|
| Wasser ..... | 100 ccm, |
| Wasserfreies Natriumsulfit ..... | 5 g, |
| Amidol ..... | 1 g, |
| Fixiernatron ..... | 2·5 g, |
| Bromkalium (1 : 10) ..... | 10 Tropfen. |

als eine verhältnismässig gute betrachtet wurde, so kann sie doch nach unseren Untersuchungen kein genügend kräftiges Bild erzielen, ausserdem nimmt sie sehr langer Zeit, nämlich 37 bis 40 Minuten, in Anspruch für vollständige Fixierung der Platten, so dass sei keineswegs als praktisch anwendbar betrachtet werden kann.

Es wurde daher von uns versucht, einerseits die Fixierung durch einen höheren Gehalt an Fixiernatron zu beschleunigen, andrerseits die Bildkraft durch den vermehrten Zusatz von Amidol zu steigern. Vermehrt man den Gehalt an Fixiernatron in der vorstehenden Cré-

1 Photo-Revue, **26**, 170 (1911).

2 Jahrb. Phot. Reprod., **26**, 6 (1912).

mierschen Vorschrift, wird die Zeit zur vollständigen Ausfixierung einigermassen abgekürzt, nämlich es braucht mit 5% Fixiernatron circa 20 bis 21 Minuten, mit 6% 13 bis 14 Minuten, mit 7% 13 bis 14 Minuten, mit 8% 12 bis 13 Minuten, bei der Temperatur zwischen 18° und 23°C, doch macht sich die bekannte verzögernde Wirkung unliebsam bemerkbar und die Dichtigkeit des entwickelten Bildes nimmt mit dem zunehmenden Fixiernatron-Gehalt stark ab, wenn auch der Amidol-Gehalt bis zum 3% vermehrt wird. Es ist uns also leider nicht gelungen, mit Amidol solchen Fixier-Entwickler herzustellen, welcher die Platte in kurzer Zeit ausfixiert und dem Bild genügende Dichtigkeit geben würde; daher wurden andere Entwicklungs-substanzen der Prüfung unterworfen.

Zuerst wurde der von 0·5 g Metochinon, 3 g wasserfreiem Natriumsulfit, 0·5 g wasserfreiem kohlensaures Natron und 100 ccm Wasser bestehende Metochinon-Entwickler unter Zusatz von verschiedener Menge Fixiernatron untersucht. Mit 5% Fixiernatron brauchte es circa 20 bis 21 Minuten, mit 6% 13 bis 14 Minuten, mit 7% 13 bis 14 Minuten, mit 8% 12 bis 13 Minuten, mit 9% 11 bis 12 Minuten, mit 10% 8 bis 10 Minuten für vollstandige Ausfixierung der Platten; in jedem Falle zeigten die Platten sehr geringe Schwärzung an Höchste-Lichtern und die Schatten-Details wurden gänzlich zerstört, so dass man mit solchem Entwickler kein kopierfähiges Negativ bekommen kann.

Da, wie obige Versuche zeigen, die für vollständige Ausfixierung der Platten nötige Zeit bei dem Fixiernatron-Gehalt von 6% bis 8% nicht stark variiert und bei einer über 9% Fixiernatron enthaltenden Lösung eine sehr energische verzögernde Wirkung sich zeigt, so wurde eine 6% Fixiernatron, 0·5% wasserfreies kohlensaures Natron und 3% wasserfreies Natriumsulfit enthaltende Flüssigkeit unter zunehmendem Zusatz von Metochinon der Untersuchung unterworfen, doch sind keine grossen Schwärzungsunterschiede an Höchste-Lichtern bei den über 0·6% Metochinon enthaltenden Elüssigkeiten bemerkbar.

Es wurde nun die 0·6% Metochinon, 3% wasserfreies Natriumsulfit, 6% Fixiernatron und 0·6% wasserfreies kohlensaures Natron enthaltende Lösung genommen und der Gehalt an kohlensaurem Natron bis 1·1% vermehrt. Keinesfalls gab es doch genügende Kraft an Höchste-Lichten des Bildes.

Mit kohlensaurem Kali statt kohlensauren Natrons wurden dieselben Versuche wie oben durchgeführt. Kohlensaures Kali mit Meto-

chinon, Natriumsulfit und Fixiernatron arbeiten etwas kräftiger als kohlensaures Natron, aber in allen Fällen sind die entwickelten Negative so kraftlos dass man von ihnen keine gute Kopie erhalten kann.

Es muss also aus den vorstehenden Versuchen geschlossen werden, dass das Metochinon mit kohlensauren Alkali und Fixiernatron keinen brauchbaren Fixier-Entwickler gibt.

Setzt man doch Aetznatron in geeigneter Menge in die Metochinon=, Natriumsulfit= und Fixiernatron= haltige Lösung, so bekommt man eine rasch fixierte, kräitig und klar arbeitende Flüssigkeit.

Wir haben verschiedene Zusammensetzungen von Metochinon, Natriumsulfit, Fixiernatron und Aetznatron untersucht, und es ergab sich die folgende Zusammensetzung als die beste:

| | | |
|---|---|---|
| Wasser | 100 ccm, | Entw. Temp. 18° bis 22°C. |
| Metochinon | 0·6 g, | |
| Wasserfreies Natriumsulfit | 3 g, | |
| Aetznatron | 0·5 g, | |
| Fixiernatron | 6 g. | |

Mit diesem Fixier-Entwickler kommt das Bild augenblicklich in Augenschein und bekommt nach 1 bis 1½ Minuten vollen Kraft.

Vermehrt man den Gehalt an Fixiernatron im vorstehenden Rezepte, so nimmt die Dichtigkeit des Bildes ab, aber die Fixierungszeit wird abgekürzt. Vermindert man den Gehalt an Aetznatron, so bekommt man keine genügende Schwärzung an Höchste-Lichtern und die Platten zeigen unangenehme braune Schleier.

Es ist empfehlenswert Metochinon und Aetznatron in getrennter Lösung zu präparieren und vor dem Gebrauch beides zu mischen.

Wir geben als praktisches Rezept das folgende an:—

| | | |
|---|---|---|
| Lösung A | Wasser | 60 ccm, |
| | Metochinon | 06· g, |
| | Wasserfreies Natriumsulfit | 3 g, |
| Lösung B | Wasser | 40 ccm, |
| | Fixiernatron | 6 g, |
| | Aetznatron | 0·5 g. |

Vor dem Gebrauch werden 3 Vol. Lösung A und 2 Vol. Lösung B gemischt.

Dieser Fixier-Entwickler arbeitet etwas hart.

Dasselbe haben wir zwar mit Hydrochinon und mit Metol untersucht, sind wir jedoch leider zu keinem zweckmässigen Rezepte gelangt.

# On the Beckmann Rearrangement. IV.

## Acyl Derivatives of the Substituted Imido-Acids.

By

**Mitsuru Kuhara and Kanoichiro Suitsu.**

(Received July 6, 1914.)

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It is almost evident that the intermediate formation of the acyl derivatives of the substituted imido-acids is a necessary condition of the Beckmann rearrangement of the ketoximes by the acid chlorides, acids, etc., as has been often mentioned in the previous articles[1] by one of us (M.K.) and his collaborators. Expecting that the isolation and synthesis of such compounds, if possible, may throw some more light upon the nature of the Beckmann rearrangement, an investigation for such a direction has been attempted as a subject of particular interest.

Wheeler and Johnson[2] have explained the formation of diacylanilides by the action of acyl chlorides upon the silver salts of acylanilides. Mumm[3] has synthesized several acylbenzanilides by shaking an etherial solution of phenylbenzimido-chloride (benzanilidimide chloride)[4] together with the aqueous solutions of the sodium salts of several organic scids. The actual isolation, however, of the acyl derivatives of the substituted imido-acids (pseudoamides), which would seem to be the intermediate products of the reactions, has not been effected.

Carrying out an experiment suggested by one of us (M.K.), Kodama has succeeded to isolate a compound which may be considered to be formed from diphenylketoxime through the Beckmann rearrangement by acetyl chloride, and must possess the constitution corresponding to phenylbenzimido-acetate[5].

$$\begin{array}{l} C_6H_5.C.OCO.CH_3 \\ \quad\quad\quad\

by treating an etherial solution of phenylbenzimido-chloride with silver acetate. The substance is a thick yellow oil of unstable nature, and forms its hydrochloride as a canary yellow precipitate by passing dry hydrochloric acid through its etherial solution cooled with a freezing mixture, but by the excess of the acid changes to acetylbenzanilide,[1] probably by the secondary reaction, The hydrochloride dissolved in chloroform and heated above 60° yields benzanilide at once. When sodium acetate is used for its preparation instead of silver acetate, the product always consists entirely of acetylbenzanilide. Then, the reactions for the formation of phenylbenzimido-acetate and for the decomposition of its hydrochloride into benzanilide shall be represented as follows :

$$\underset{\text{Phenylbenzimido-chloride. Faintly yellow.}}{C_6H_5.C(=N.C_6H_5).Cl} \quad AgOCO.CH_3 \longrightarrow \underset{\text{Phenylbenzimido-acetate. Yellow.}}{C_6H_5.C(=N.C_6H_5).OCO.CH_3}$$

$$\underset{\text{Hydrochloride of phenylbenzimido-acetate.}}{C_6H_5.C(=HCl,N.C_6H_5).OCO.CH_3} \longrightarrow \underset{\text{Benzanilide.}}{C_6H_5CO.HN.C_6H_5} + \underset{\text{Acetyl chloride,}}{ClCO.CH_3}$$

And the production of acetylbenzanilide may be the result of the secondary reaction or of the intramolecular rearrangement noticed by Mumm.[2]

Now the last phase of the Beckmann rearrangement of diphenylketoxime by acetyl chloride is highly probable to be due to the above-mentioned decomposition of the hydrochloride of phenylbenzimido-acetate which is assumed to be formed as an intermediate product in the rearrangement of diphenylketoxime acetyl ester formed in reaction, being inferred from its behaviours ; so for convenience the whole scheme of the Beckmann rearrangement, as it is assumed, shall be stated again :

$$C_6H_5.C(=N.OH).C_6H_5 + CH_3.COCl \longrightarrow \left[C_6H_5.C(=HCl,N.OCO.CH_3).C_6H_5\right] \longrightarrow$$

$$\left[C_6H_5.C(=HCl,N.C_6H_5).OCO.CH_3\right] \longrightarrow C_6H_5.CO.HN.C_6H_5 + CH_3.COCl$$

1 Amer. Chem. J., 18, 546 (1896).

2 Loc. cit.

It is, however, not possible to isolate phenylbenzimido-acetate as an intermediate product from diphenylketoxime acetyl ester by its intramolecular rearrangement, as the latter does not undergo the rearrangement by itself even by the rise of temperature, on account of the weak negative character of the acetic acid residue present, but always the aid of hydrochloric acid is needed for its rearrangement as has been often stated. When hydrochloric acid is present, therefore, phenylbenzimido-acetate formed would yield its hydrochloride, and its decomposition may progress until the extreme so that its isolation as an intermediate product is not possible.

Nevertheless, diphenylketoxime benzenesulphonyl ester actually undergoes the spontaneous rearrangement without the aid of any reagent, owing to the presence of the strong negative acid residue, with the formation of phenylbenzimido-benzenesulphonate whose isolation is posssible, the scheme of rearrangement being represented here again:

$$\begin{array}{l} C_6H_5.C.C_6H_5 \\ \quad\quad\| \\ \quad N.OSO_2.C_6H_5 \end{array} \longrightarrow \begin{array}{l} C_6H_5.C.OSO_2.C_6H_5 \\ \quad\quad\| \\ \quad N.C_6H_5 \end{array}$$

In fact, phenylbenzimido-benzenesulphonate has been isolated by one of us (M. K.) and Matsunami from diphenylketoxime benzenesulphonyl ester by rearrangement, and an account has been preliminarily communicated to the Memoirs of the College of Science and Engineering[1].

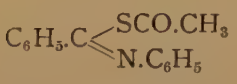
As has been already mentioned, it is not only difficult to isolate phenylbenzimido-acetate as an intermediate product of the rearrangement of diphenylketoxime by acetyl chloride, but also it is a hard task to prepare it synthetically in a perfectly pure state by the action of metallic acetate upon phenylbenzimido-chloride without exception, often resulting only in the production of benzanilide and acetylbenzanilide; so we are not able to catch a just right condition for the constant formation of the yellow oil or phenylbenzimido-acetate. The authors, have, therefore, attempted to synthesize the other esters of the same type by the action of the metallic salts of the other acids upon phenylbenzimido-chloride, in order to see if the actual isolation of the esters of such a kind as phenylbenzimido-acetate is possible. For this purpose, at first the synthesis of phenylbenzimido-thioacetate was carried out, fortunately with success. In this experiment, potassium thioacetate,

1 Mem. Coll. Sci. Engin., Kyoto, **6**, 7 (1913).

$KS.CO.CH_3$. was made to react with phenylbenzimido-chloride, dissolved in petroleum ether in presence of anhydrous potassium carbonate at the ordinary temperature, by which process the yellow coloration of the solution was at first observed, followed by its gradual change to orange red. On allowing the solution to stand for several days, yellow crystals were found to deposit mixed with some orange red crystals; and two substances were separated by fractional crystallization and each analysed. Both substances possess the same composition corresponding to the impirical formula $C_{15}H_{13}NOS$.

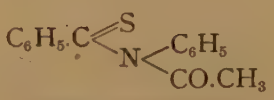
It is now concluded that the yellow conpound would be phenylbenzimido-thioacetate possessing the constitution represented by the formula I, and the orange red substance would be acetylphenylthiobenzamide having the formula II:

I



Phenylbenzimido-thioacetate.

II



Acetylphenylthiobenzamide.

interpreting from the facts which will be described hereinafter:

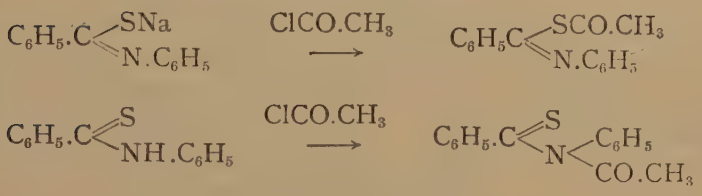
1. When the perfectly pure phenylbenzimido-chloride is allowed to interact with potassium thioacetate, the yellow compound alone is formed, not a trace of the orange red compound being observed to be formed.

2. The yellow compound changes to the orange red isomer, when comes in contact with phosphorus oxychloride, acetyl chloride, benzoyl chloride, alkali, etc., or when kept in a vessel filled with hydrochloric acid gas. It is then assumed that the yellow compound is the primary reaction-product of phenylbenzimido-chloride and thioacetate, which may secondarily change to the orange red isomer by the aid of the acid possibly present in the chlorides used or by alkali:

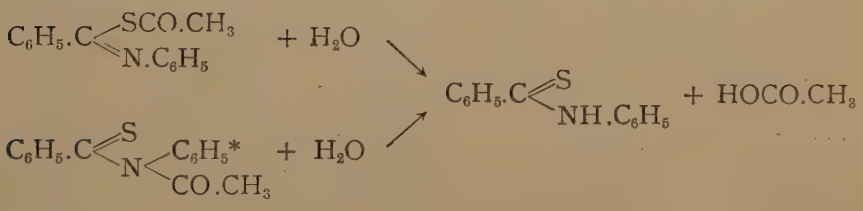
3. The formula I indicates the presence of a chromophoric group, $>C=N.C_6H_5$, which is assumed to give rise to the manifestation of yellow colour.[1]

4. Acetyl chloride, when react with sodium salt of thiobenzanilide suspended in xylene, yields a considerable amount of the yellow compound, while in a dry etherial solution of thiobenzanilide in presence of anhydrous potassium carbonate it produces the orange red compound; the reactions in both cases should be represented as follows:

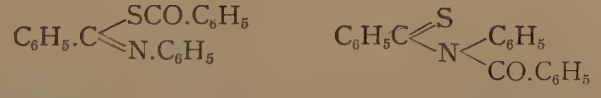
[1] Mem. Coll. Sci. Engin., Kyoto, **2**, 366 (1909–1910).



5. Subjecting both yellow and orange red compounds to hydrolysis by means of dilute acid or alkali, they are decomposed yielding the same products, that is, thiobenzanilide and acetic acid. Such phenomena of decomposition may be shown by the following scheme:



Continuing experiment further with potassium (or silver) thiobenzoate and phenylbenzimido-chloride under the same condition, it has also been noticed that both yellow and orange red compounds are produced as in the other case. Their behaviours are similar with those of the corresponding thio-compounds above mentioned; hence by analogy their respective constitutional formulas should be represented as follows:



Phenylbenzimido-thiobenzoate. Yellow.

Benzoylphenylthiobenzamide. Orange red.

In conclusion it may be said that the existence of the esters of the types, $C_6H_5.C.(OCOR):N.C_6H_5$, $RC(OSO_2.C_6H_5):NR$ and $C_6H_5.C.(SCOR):N.C_6H_5$ (in which $R=C_6H_5$ or $CH_3$) is possible, and that the esters corresponding to the first two formulas would be formed as the intermediate products of the Beckmann rearrangement of the respective ketoximes by the respective acid chlorides, inferring from their behavi-

* In the mixed diacylanilides, the lower acyl group is removed according to Wheeler, Smith and Warren's view.—Amer. Chem. J., **19**, 758 (1897).

ours as well as from their actual isolation in the course of rearrangement. Especially, the investigation with regard to the rearrangement of benzenesulphonyl esters of ketoximes is now going on in our laboratory.

## EXPERIMENTAL PART.

### 1 *Action of Silver Acetate upon Phenylbenzimido-chloride.*

A slight excess of finely powdered anhydrous silver acetate over an equivalent quantity was added by small quantities to a well cooled etherial solution of phenylbenzimido-chloride (benzanilidimide chloride) prepared according to Wallach's statement,[1] with constant and vigorous shaking of the mixture. At the beginning of reaction the white silver salt turned yellow on its surface, but the liquor soon got yellow, gradually increasing in depth, as the yellow substance formed passes into solution. The etherial solution was then filtered, and ether removed by evaporation quickly passing a current of dry air. In the course of evaporation, there separated out at first some platy crystals which were confirmed to be benzanilide by its characteristic properties, soon followed by the deposition of colourless needle-shaped crystals and finally there remained a thick yellow oil. The needle-shaped crystals purified by repeated recrystallization from petroleum ether and also from dilute alcohol were found to melt at 63.5° and to possess all the properties of acetylbenzanilide already obtained by Wheeler and McFarland[2]. The oil was then treated with petroleum ether for its purification, and the solution, was allowed to evaporate by passing a current of dry air. Its analysis has not been conducted, as the substance is very difficult to be obtained in a perfectly pure state on account of its changeble character, yet the substance should undoubtedly be phenylbenzimide-acetate, $C_6H_5.C.(OCO.CH_3):N.C_6H_5$, being inferred from its behaviours.

By passing a current of dry hydrochloric acid through an etherial solution of the oil cooled with a freezing mixture, its hydrochloride separated out as a canary yellow precipitate which can be reconverted into the original substance by means of anhydrous potassium carbonate. The hydrochloride, when exposed to moist air, soon changed reddish brown, with the formation of benzanilide, aniline and acetic acid as its

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1 Lieb. Ann., **184**, 79 (1877).

2 Amer. Chem. J., **18**, 546 (1896).

decomposition products. Heating the hydrochloride dissolved in dry chloroform in a sealed tube above 60° for about half an hour, it was found to be transformed into benzanilide. The oil itself alone dissolved in chloroform or benzene, when heated in a sealed tube at 160–170° for about two hours showed no perceptible change. It readily decomposes by acid and alkali splitting up into acetic acid (or its salt) and benzanilide.

### 2. *Action of Sodium Acetate and of Silver Benzoate upon Phenylbenzimido-chloride.*

Gently warming an etherial solution of phenylbenzimido-chloride mixed with some powdered anhydrous sodium acetate, and then evaporating the solution, the residue was extracted with petroleum ether, by which process acetylbenzanilide[1] was isolated without the intermediate formation of the yellow isomer.

By the action of silver benzoate upon phenylbenzimido-chloride dissolved in ether, a yellow oil and needle-shaped crystals were isolated besides benzanilide and some benzoic acid. The needle-shaped crystals were found to be dibenzoylanilide[2], as it possesses the melting point of 155° (Losanitsch) and all its characteristic properties. The yellow oil should be phenylbenzimido-benzoate, since its formation and decomposition are wholly analogous with those of the acetyl ester obtained from silver acetate and phenylbenzimido-chloride.

The formation of acetyl- and dibenzoylanilides in those cases above described may be due to the rearrangement noticed by Mumm.

### 3. *Action of Potassium Thioacetate upon Phenylbenzimido-chloride.*

Finely powdered anhydrous potassium thioacetate was added to a dry petroleum ether solution of phenylbenzimido-chloride previously mixed with some anhydrous potassium carbonate in order to avoid the action of acid which is possible to be present, and the mixture was constantly shakened for a while at the ordinary temperature. At the beginning of reaction, the surface of potassinm thioacetate was covered

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1 Loc. cit.

2 Refer Beilstein II, 1171. Ber. D. chem. Ges., **43**, 886 (1910).

with a yellow coating, but the solution soon changed pink, followed by the gradual increase of the depth of colour. On allowing the mixture to stand for a few days with occasional shaking, the yellow coloured phenylbenzimido-thioacetate was found to deposit, mixed with the orange red crystals of acetylphenylbenzamide. The mixture was filtered, and the residue treated with warm petroleum ether and the solution concentrated by distillation under a diminished pressure. Letting the concentrated solution stand for a while there separated out a mass of granular orange red crystals. The substance purified by recrystallization from dry petroleum ether, consists of deep orange red coloured needles, and melts at 78·5–79·5°. It is soluble in common organic solvents with dark orange red colouration. Its analysis gave the following values for sulphur:

I. 0·2384 grm. substance gave 0·222 grm. $BaSO_4$.
II. 0·2576 „ „ „ 0·237 „ „
III. 0·1860 „ „ „ 0·171 „ „

| | Calculated for $C_6H_5.C.(N.C_6H_5.CO.CH_3):S$ | Found I | II | III |
|---|---|---|---|---|
| Sulphur | 12·57 | 12·75 | 12·64 | 12·63 |

Warming with dilute acid or alkali, it is readily transformed into thiobenzanilide melting at 97·5–98·5°.

The last residue left after extracting with petroleum ether was treated with chloroform, and the solution thus obtained was allowed to evaporate by passing a current of dry air; the residue consisting of phenylbenzimido-thioacetate was repeatedly washed with cold absolute alcohol and then dissolved in a mixture of chloroform and ether. On allowing the solution to stand for a while there deposited a lot of monoclinic amber-yellow coloured crystals.

The analysis of the substance gave the following values for sulphur:

I. 0·1530 grm. substance gave 0·1406 grm. $BaSO_4$.
II. 0·2402 „ „ „ 0·2172 „ „

| | Calculated for $C_6H_5.C(SCO.CH_3):N.C_6H_5$ | Found I | II |
|---|---|---|---|
| Sulphur | 12·57 | 12·62 | 12·41 |

[1] Ber. D. chem. Ges., **43**, 886, 3336 (1910).

Phenylbenzimido-thioacetate is of rather stable nature, difficultly soluble in alcohol, ether, petroleum ether, benzene and acetone, but readily in chloroform. By boiling with alcohol or warming with acid or alkali it is transformed into thiobenzanilide with more difficulty than its isomer, acetylphenylthiobenzamide. The yellow crystals of phenylbenzimido-thioacetate, when heated, melt to a deep orange red liquid, which solidifies to the original yellow substance when cooled. The substance being brought in contact with phosphorus oxychloride, acetyl chloride, benzoyl chloride or caustic alkali, or being kept under a desiccator filled with dry hydrochloric acid gas, is transformed into the orange red isomer. In the latter case, the reaction progresses until the extreme so as to produce thiobenzanilide, when it is allowed to stand for several days. On boiling the substance with water no perceptible change is observed to take place. Purer the phenylbenzimido-chloride used is, the less acetylphenylthiobenzamide is produced; thus when potassium thioacetate is allowed to react with the well purified phenylbenzimido-chloride, phenylbenzimido-thioacetate alone is observed to be formed without the addition of potassium carbonate. From such a relation, it is almost evident that phenylbenzimido-thioacetate formed as a primary product of reaction would change to isomeric acetylphenylthiobenzamide by the action of acid, which is probable to be mixed with the impure phenylbenzimido-chloride, being derived from phosphorus oxychloride, acid chlorides, etc. used.

### 4. *Action of Acetyl Chloride upon Thiobenzanilde and upon its Sodium Salt.*

On adding an etherial solution of an equivalent quantity of the purified acetyl chloride to an etherial solution of thiobenzanilide in presence of anhydrous potassium carbonate, the solution was soon observed to alter deep orange red under the evolution of carbon dioxide. Evaporating the solution by passing a current of dry air through it, there was left an orange red substance; and from the petroleum ether solution of the latter the orange red coloured crystals separated out and were found to possess all the properties of acetylphenylthiobenzamide, $C_6H_5.C.(N.C_6H_5.COCH_3):S$.

1 gram of metallic sodium was added to 9 grams of thiobenzanilide dissolved in 100 grams of dry xylene, and the mixture was heated for 15 hours in a flask provided with an inverted condenser over an oil

bath at the temperature of 110–120°. When the reaction ended, the whole contents were cooled, and 20 c.c. of 1 molar solution of acetyl chloride in xylene were gradually added from a burette. At first there deposited some phenylbenzimido-thioacetate alone, then the solution getting orange red. Driving off xylene from the mother liquor by continually passing a current of dry air for several days, phenylbenzimido-thioacetate was left as a residue together with some orange red isomer and colourless crystals. The whole residue, by treating with cold absolute alcohol, left the yellow crystals of phenylbenzimido-thioacetate undissolved. The solubility, crystalline form and chemical properties of the substance show that it is identical with phenylbenzimido-thioacetate, $C_6H_5.C.(SCO.CH_3):N.C_6H_5$, obtained from phenylbenzimido-chloride and sodium thioacetate.

### 5. *Action of Potassium Thiobenzoate upon Phenylbenzimido-chloride.*

By the action of potassium thiobenzoate upon phenylbenzimido-chloride dissolved in dry petroleum ether in presence of anhydrous potassium carbonate at the ordinary temperature, there deposited some yellow compound at first, followed by the gradual increase of the depth of red colour of the mother liquor. Allowing the mixture to stand for a month, a lot of yellow compound was found to crystallize out together with some orange crystals. Two compounds were separated by the similar treatment as in the case of two analogous acetyl derivatives of thiobenzanilide mentioned before.

The orange red compound is soluble in common organic solvents, melts at 110–111° and decomposes into thiobenzanilide and benzoic acid by heating with dilute acid or alkali. The analysis of the substance gave the following value for sulphur:

0·2371 grm. substance gave 0·1684 grm. $BaSO_4$.

| | Calculated for $C_6H_5.C.(SCO.C_6H_5):N.C_6H_5$ | Found |
|---|---|---|
| Sulphur | 10·11 | 9.76 |

Accordingly the orange red compound would be no doubt benzoyl-phenylthiobenzamide, and as the yellow one is similar to phenylbenzimido-thioacetate in all respects, so it should be phenylbenzimido-thiobenzoate, $C_6H_5.C.(SCO.C_6H_5):N.C_6H_5$.

# Determination of Very Weak Acids and Bases by Means of Electrolytic Conductivity Measurements.

By

**Shinkichi Horiba.**

(Received July 6, 1914.)

As is well known, the ordinary method of acidimetry and alkalimetry is not applicable to the determination of very weak acids and bases. Preliminary experiments gave evidencc that in such a case electrolytic conductivity measurement might conveniently be used; and the method of procedure has been investigated.

## A. The Electrolytic Conductivity of a Mixture of a Weak Base and a Strong Acid.

As representative of a weak base aniline was chosen, and the electrolytic conductivities of mixtures of aniline and hydrochloric acid in different proportions were measured in the following way.

20 cc. of hydrochloric acid of a known concentration were mixed with 5 cc. of an aqueous solution of aniline in different concentrations, the mixture was put in a conductivity vessel which was immersed in a thermostat at 25·0°C. and the electrolytic conductivities were determined. Ordinary distilled water was used in the preparation of these solutions, because the specific conductivity of the distilled water in our laboratory was less than $4.10^{-6}$ reciprocal ohms, and this order of conductivity was negligible for the present investigation.

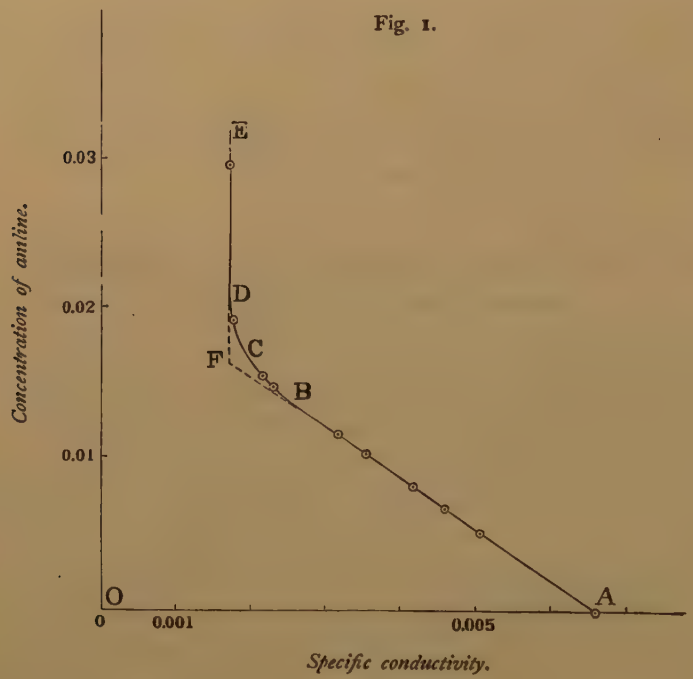
TABLE I.

| Concentration of aniline used. | Concentration of aniline in conductivity vessel. | Concentration of hydrochloric acid in conductivity vessel. | Specific conductivity. |
|---|---|---|---|
| 0 | 0 | 0·01645 | 0·006653 |
| 0·02603 | 0·005206 | „ | 0·005119 |
| 0·03472 | 0·006944 | „ | 0·004590 |

| | | | |
|---|---|---|---|
| 0·04166 | 0·008332 | 0·01645 | 0·004156 |
| 0·05207 | 0·01041 | „ | 0·003505 |
| 0·05946 | 0·01189 | „ | 0·003077 |
| 0·07425 | 0·01485 | „ | 0·002284 |
| 0·07680 | 0·01536 | „ | 0·002150 |
| 0·09670 | 0·01934 | „ | 0·001730 |
| 0·1485 | 0·0297 | „ | 0·001697 |

The curve representing the change of the specific conductivity of the mixture with the change of the aniline concentration is shown in Fig. 1, specific conductivity being taken as abscissa and concentration

Fig. 1.




of aniline as ordinate. As seen in the figure, the specific conductivity of the solution is a linear function of the concentration of aniline, becoming smaller and smaller as the concentration increases. This is represented by a straight line *AB*, *OA* being the specific conductivity of the pure hydrochloric acid solution. When the concentration of aniline approaches that of the hydrochloric acid, however, the rate of decrease of the conductivity becomes greater and greater and the straight line turns to a curve convex to the axes, as *BCD*. When

aniline is present in excess, the specific conductivity varies very slightly with its concentration; and the relation is again represented by a straight line *DE*, which is almost parallel to the ordinate axis. The point *F*, the intersection of the elongations of the two straight lines *AB* and *DE*, is the point corresponding to a concentration of aniline exactly equivalent to the hydrochloric acid in the solution.

Now let $\varkappa_m$ and $\varkappa_a$ be respectively the specific conductivities of the mixture and the pure acid solution, and $C_b$ be the concentration of the base added; then the straight line *AB* in Fig. 1. may be represented by an equation as follows:

$$\varkappa_m = PC_b + \varkappa_a \qquad (1)$$

where $P$ is a constant. It is easily seen that the change of the conductivity of the solution with the addition of aniline is due to two different causes, firstly the conductivity is decreased by the gradual disappearance of free hydrochloric acid and secondly it is increased by the gradual formation of the neutral salt. Thus the factor $P$ must consist of the two parts corresponding to these two terms.

Since hydrochloric acid and its neutral salt may be taken as having the same dissociation degree in dilute solutions, we have the following equations:

$$\varkappa_a = \alpha_a C_a \qquad (2)$$

where $\varkappa_a$ and $C_a$ denote respectively the specific conductivity of hydrochloric acid and the concentration of the acid and $\alpha_a$ is a constant for hodrochloric acid.

Similarly we have the following expression for the neutral salt,

$$\varkappa_s = \alpha_s C_s \qquad (3)$$

when any hydrolysis of the salt is negligible.

If the relations (2) and (3) hold, the coefficient $P$ can be dissolved into two terms such as,

$$P = (-\alpha_a + \alpha_s)$$

then, we have

$$\varkappa_m = (-\alpha_a + \alpha_s)C_b + \varkappa_a. \qquad (4)$$

This equation was derived under the assumption that no hydrolytic dissociation took place, but in fact it becomes remarkable only when the free acid is greatly decreased and the curved part *BCD* of Fig. 1 is the result. When aniline is present in excess, the conduc-

tivity is almost entirely due to the neutral salt in the solution, and the conductivity, due to the free weak base itself in the presence of its neutral salt, may be neglected. This explains the fact that an excess of aniline has no noticeable effect on the conductivity of the solution.

*Calculation of the Factor $a_a$.*

TABLE II.

| Concentration of hydrochloric acid. | Specific conductivity. | $a_a = \frac{\varkappa_a}{C_a}$ | Concentration of hydrochloric acid (calc.). |
|---|---|---|---|
| 0·03296 | 0·01314 | 0·400 | 0·03252 |
| 0·01645 | 0·006635 | 0·405 | 0·01643 |
| 0·01028 | 0·004190 | 0·408 | 0·01037 |
| 0·00685 | 0·002819 | 0·412 | 0·00698 |

The factor $a_a$ changes a little with the concentration of the acid; but taking $a_a$ as a constant, say $a_a \doteqdot 0{\cdot}404$, the calculated values of the concentrations from the observed specific conductivities are not very different from the actual values, as shown in the 4th column of Table II. For equation (4), however, the observed value and not $0{\cdot}404 \times C_a$ must be used, because a small error in $\varkappa_a$ will remarkably affect the calculated concentration of the base.

*Calculation of the Factor $a_s$.*

If the relation (4) holds for the point $F$, which is the intersection of the two straight lines, and represents concentration of aniline equivalent to the hydrochloric acid in the mixture, we get the following relation:

$$\varkappa_a - a_a C_b = 0$$

and the equation (4) becomes:

$$\varkappa_m = a_s C_b = a_s C_a.$$

As the straight line $EF$ is almost parallel to the ordinate axis, the conductivity of the mixture may be put equal to $\varkappa_m$ in the above equation when large excess of aniline is present, and thus the value of $a_s$ is easily found.

The specific conductivity of the mixture formed from 20 cc. of hydrochloric acid of 0·02056 norm. and 5 cc. of aqueous solution of aniline of 0·09676 norm. was 0·00173 reciprocal ohms, therefore we have

$$0.00173 = a_s \frac{0.02056 \times 4}{5}$$

$$a_s = 0.105.$$

Again, the specific conductivity of the mixture formed from 20 cc. of hydrochloric acid of 0·05120 norm. and 5 cc. of aqueous aniline solution of 0·1934 norm. was 0·00349 reciprocal ohms, therefore we have

$$0.00349 = a_s \frac{0.04120 \times 4}{5}$$

$$a_s = 0.106.$$

Thus we may put as the mean

$$a_s = 0.1055$$

then $$P = -a_a + a_s = -0.404 + 0.1055$$

$$= -0.2985.$$

Lastly we have the equation:

$$\varkappa_m = -0.2985\ C_b + \varkappa_a.$$

*The Experimental Verification of the Equation.*

TABLE III.

The concentration of hydrochloric acid used: 0·04120.

The concentration of hydrochloric acid in the conductivity vessel:

$$\frac{4}{5} \times 0.04120 = 0.03296.$$

The specific conductivity of the acid: 0·01314.

Therefore

$$\varkappa_m = -0.2985\ C_b + 0.01314.$$

| Concentration of aniline used. | Concentration of aniline in cond. vessel. | Specific conductivity. | Concentration of aniline (calc.). | Error. |
|---|---|---|---|---|
| 0·09670 | 0·01934 | 0·007345 | 0·01942 | +0·00006 |
| 0·06447 | 0·01289 | 0·009224 | 0·01306 | +0·00017 |

TABLE IV.

The concentration of hydrochloric acid used : 0·02056.

The concentration of hydrochloric acid in the conductivity vessel :

$$\frac{4}{5} \times 0{\cdot}02056 = 0{\cdot}01645.$$

The specific conductivity of the acid : 0·006635.

Therefore

$$\varkappa_m = -0{\cdot}2985\ C_b + 0{\cdot}006635.$$

| Concentration of aniline used. | Concentration of aniline in cond. vessel. | Specific conductivity. | Concentration of aniline (calc.) | Error. |
|---|---|---|---|---|
| 0·02603 | 0·005206 | 0·005119 | 0·005140 | −0·000066 |
| 0·03472 | 0·006944 | 0·004590 | 0·006911 | −0.000033 |
| 0·04166 | 0·008332 | 0·004156 | 0·008366 | +0·000034 |
| 0·05207 | 0·010414 | 0·003505 | 0·01054 | +0·00013 |

As seen from the above tables, the agreements between observed and calculated values are quite satisfactory.

### *Application in Chemical Analysis.*

From the above experiments, it is evident that a weak base such as aniline, which can not be determined by the ordinary method of alkalimetry, may easily be estimated by the measurement of the conductivity of mixtures of the aniline solution and hydrochloric acid.

Let $c$ be the concentration of the aniline and $\varkappa$ be the specific conductivity of this mixture, then

$$c = -\frac{\varkappa - \varkappa_a}{0{\cdot}2895}$$

in which the observed value of $\varkappa_a$ is to be used. This equation is valid, with the constant factor 0·2895, between the limit $\frac{1}{50} - \frac{2}{50}$ norm. of hydrochloric acid, in excess of aniline. It is to be remarked here that the solution may contain some indifferent substances such as chloroform, without affecting the result.

### *Calculation of the Degree of the Hydrolysis.*

We can calculate the degree of the hydrolysis of a salt by means of equation (4).

If we have the following data:

the concentration of hydrochloric acid in the conductivity vessel: $\frac{1}{5} \times 0{\cdot}08234$,

the concentration of aniline in the conductivity vessel: $\frac{1}{5} \times 0{\cdot}07425$,

the specific conductivity of this mixture: $0{\cdot}002284$,

then $$0{\cdot}002284 = -0{\cdot}2985\, c + 0{\cdot}006635$$

$$c = 0{\cdot}07316 \times \frac{1}{5}.$$

Therefore we have:

the concentration of aniline hydrochloride in the mixture: $0{\cdot}07316 \times \frac{1}{5}$,

the concentration of free aniline: $(0{\cdot}07425 - 0{\cdot}07316) \times \frac{1}{5}$,

the concentration of free hydrocnloric acid: $(0{\cdot}08234 - 0{\cdot}07316) \times \frac{1}{5}$.

If $K$ be the constant of the hydrolysis, then

$$K = \frac{[\text{Base}][\text{Acid}]}{[\text{Salt}]} = \frac{(0{\cdot}07425 - 0{\cdot}07316)(0{\cdot}08234 - 0{\cdot}07316)}{5 \times 0{\cdot}07316}$$

$$= 2{\cdot}74 \times 10^{-5}.$$

Moreever the following results were obtained.

| Concentration of hydrochloric acid. | Concentration of aniline. | Specific conductivity. | Concentration of aniline hydrochloride (calc.). | $K$ |
|---|---|---|---|---|
| $0{\cdot}1648 \times \frac{1}{5}$ | $0{\cdot}1536 \times \frac{1}{5}$ | $0{\cdot}004063$ | $0{\cdot}1522 \times \frac{1}{5}$ | $2{\cdot}26 \times 10^{-5}$ |
| $0{\cdot}08234 \times \frac{1}{5}$ | $0{\cdot}07680 \times \frac{1}{5}$ | $0{\cdot}002150$ | $0{\cdot}07543 \times \frac{1}{5}$ | $2{\cdot}51 \times 10^{-5}$ |

The constant of the hydrolysis of aniline hydrochloride at 25·0°C. given in literature is as follows:

| | |
|---|---|
| $2{\cdot}25 \times 10^{-5}$ | Bredig[1] |
| $2{\cdot}29 \times 10^{-5}$ | Denison and Steele[2] |
| $2{\cdot}16 \times 10^{-5}$ | Denham[3] |

1 Zs. physik. Chem., **13**, 322 (1894).

2 J. Chem. Soc., **89**, 1008 (1906).

3 *Ibid.*, **93**, 48 (1908).

## B. The Electrolytic Conductivity of a Mixture of a Weak Acid and a Strong Base.

As representative of a weak acid phenol was taken, and the conductivities of the mixtures of phenol and sodium hydroxide were studied in the same way as the mixture of aniline and hydrochloric acid. In this case, however, distilled water free from carbonic acid was used and during the operations of the conductivity measurement, the utmost care was taken to avoid the absorption of carbonic acid from the air. The experiments were carried out in a thermostat at 25·0°C.

TABLE V.

The concentration of sodium hydroxide in conductivity vessel: $0{\cdot}04809 \times \frac{4}{5} = 0{\cdot}03847$.

| Concentration of phenol used. | Concentration of phenol in conductivity vessel. | Specific conductivity. |
|---|---|---|
| 0 | 0 | 0·008570 |
| 0·02085 | 0·004190 | 0·007866 |
| 0·04171 | 0·098342 | 0·007206 |
| 0·06202 | 0·012404 | 0·006527 |
| 0·07657 | 0·015314 | 0·006089 |
| 0·08341 | 0·016682 | 0·005865 |
| 0·09305 | 0·01861 | 0·005546 |
| 0·1407 | 0·02814 | 0·004111 |
| 0·1532 | 0·03064 | 0·003762 |
| 0·1914 | 0·03828 | 0·002981 |
| 0·3063 | 0·06126 | 0·002732 |
| 0·3311 | 0·06622 | 0·002720 |
| 0·4253 | 0·08506 | 0·002642 |

TABLE VI.

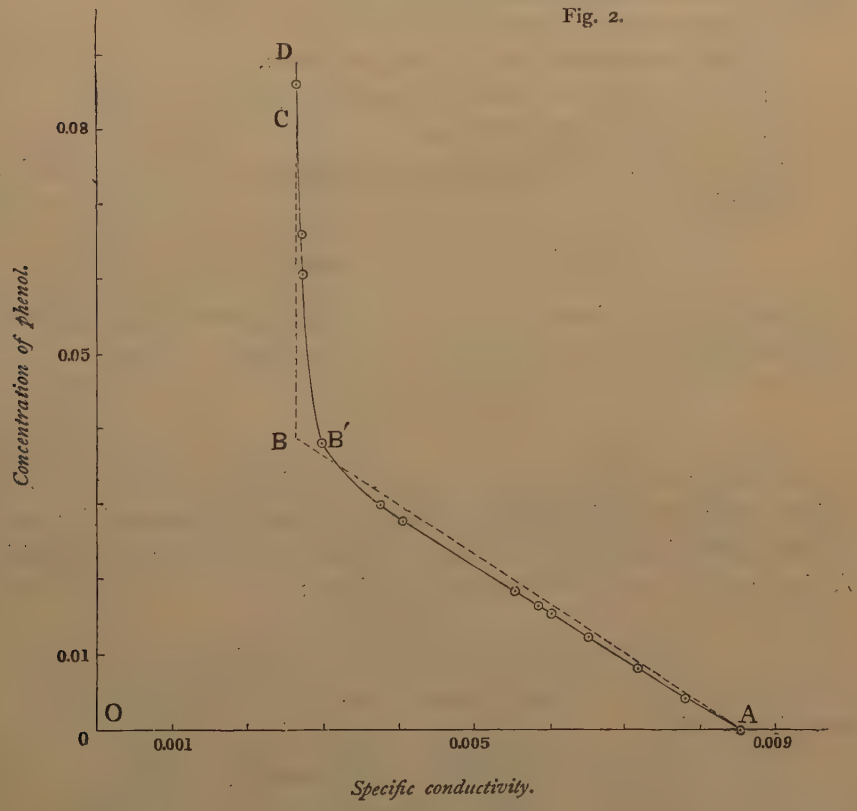
The conductivity of sodium hydroxide in conductivity vessel: $0{\cdot}02405 \times \frac{4}{5} = 0{\cdot}01924$.

| Concentration of phenol used. | Concentration of Phenol in conductivity vessel. | Specific conductivity. |
|---|---|---|
| 0 | 0 | 0·004363 |
| 0·01668 | 0·003336 | 0·003826 |

| | | |
|---|---|---|
| 0·02085 | 0·004170 | 0·003673 |
| 0·04171 | 0·008342 | 0·003034 |
| 0·04652 | 0·009304 | 0·002844 |
| 0·07657 | 0·015314 | 0·001951 |
| 0·09305 | 0·01861 | 0·001599 |
| 0·1407 | 0·002814 | 0·001437 |
| 0·3311 | 0·06622 | 0·001405 |
| 0·5683 | 0·11366 | 0·001396 |

The curve representing the change of the specific conductivity of the mixture with the change of the phenol concentration is shown in Fig. 2. The decrease of the specific conductivity with the increase of

Fig. 2.




the concentration of phenol is not rectilinear, as shown $AB'C$ in the figure; and the curve proceeds parallel to the axis of ordinate as $CD$. Now elongate the straight line $DC$ to the point $B$ which corresponds to a concentration of phenol exactly equivalent to the concentration

of sodium hydroxide in the mixture, and connect the points $B$ and $A$; then it will be seen that the conductivity curve $AB'C$ deviates from the line $AB$ at first to the left and then to the right as the concentration of phenol increases. These deviations may perhaps be ascribed to two causes, namely the hydrolysis of sodium phenolate and the slightness of the electrolytic dissociation of sodium phenolate in an excess of the hydroxide, compared to that of the free base. From an assumption that the hydrolysis is negligible, we can derive a formula for the conductivity of the mixture as follows:

$$\varkappa_m = PC_a + (C_b - C_a)^n \beta C_a + \varkappa_b \qquad (5)$$

where $\varkappa_m$ denotes the specific conductivity of the mixture,

$C_a$: the concentration of phenol,

$C_b$: the concentration of sodium hydroxide,

$\varkappa_b$: the specific conductivity of sodium hydroxide alone,

$P$: a factor for this mixture,

and $\beta$ is a factor for the dissociation degree of sodium hydroxide solution.

*Calculation of the Factor P.*

If the concentrations of phenol and sodium hydroxide be the same in the mixture, the expression (5) may be written,

$$\varkappa_m = PC_a + \varkappa_b. \qquad (6)$$

In that case, the value of $\varkappa_m$, the specific conductivity of pure sodium phenolate, will be given from the specific conductivity of a mixture containing a large excess of phenol. From the data of Table V, the factor $P$ can be calculated as follows:

$$0.002640 = P \times 0.03847 + 0.008570$$
$$P = -0.154.$$

From Table VI

$$0.001400 = P \times 0.01924 + 0.004363$$
$$P = -0.154.$$

Therefore we can put $P = -0.154$ in the case where sodium hydroxide of $\frac{2}{50} - \frac{1}{50}$ norm. is used.

*The Experimental Verification.*

In the equation (5), if $C_a$ be smaller than $C_b$, we can expand the factor $(C_b - C_a)^n$ according the binomial theorem; and, neglecting the higher terms, we obtain approximately,

$$\varkappa_m = PC_a + \beta C_b^n + \varkappa_b$$

or

$$C_a = \frac{\varkappa_m - \varkappa_b}{P + \beta C_b^n}. \qquad (7)$$

Put $n = \frac{1}{2}$, and $\beta = 0{\cdot}0433$, then from table V

$$C_a = -\frac{\varkappa_m - 0{\cdot}008570}{0{\cdot}154 + 0{\cdot}0433 \times 0{\cdot}03848^{\frac{1}{2}}}$$

$$= -\frac{\varkappa_m - 0{\cdot}008570}{0{\cdot}1625}$$

| Concentration of phenol. | Specific conductivity. | Concentration of phenol (calc.). | Error. |
|---|---|---|---|
| 0·004190 | 0·007866 | 0·004332 | +0·00014 |
| 0·008342 | 0·007206 | 0·008396 | +0·000054 |
| 0·012404 | 0·006527 | 0·01257 | +0·00017 |
| 0·015314 | 0·006089 | 0·01527 | −0·00004 |
| 0·016682 | 0·005865 | 0·01665 | −0·050017 |
| 0·01861 | 0·005546 | 0·01861 | ±0·0 |

From Table VI, we have

$$C_a = -\frac{\varkappa_m - 0{\cdot}004363}{0{\cdot}154 + 0{\cdot}0433 \times 0{\cdot}01924^{\frac{1}{2}}}$$

$$= -\frac{\varkappa_m - 0{\cdot}004363}{0{\cdot}160}$$

| Concentration of phenol. | Specific conductivity. | Concentration of phenol (calc.). | Error. |
|---|---|---|---|
| 0·003336 | 0·003826 | 0·003357 | +0.000021 |
| 0·004170 | 0·003673 | 0·004311 | +0·00014 |
| 0·008342 | 0·003034 | 0·008310 | −0·000032 |
| 0·009304 | 0·002844 | 0·009493 | +0·00019 |

The agreements of the observed and calculated values are quite satisfactry, and therefore, if it is desired to estimate the concentration

of a dilute phenol solution, the conductivity of the mixture of the phenol solution and sodium hydroxide solution may be determined, and the concentration required calculated by the formula,

$$C_a = -\frac{\varkappa_m - \varkappa_b}{0{\cdot}154 + 0{\cdot}0433 \times C_b^{\frac{1}{2}}}$$

where $C_b$ must lie between the limit $\frac{2}{50} - \frac{1}{50}$ norm. and the concentration of phenal be less than $\frac{1}{2}\ C_b$.

*Calculation of the Degree of the Hydrolysis.*

By the graphical representations of Table V and VI, the specific conductivities of equivalent solutions of phenol and sodium hydroxide are found.

i When the concentration of sodium hydroxide is
0·03877 : $\varkappa_m = 0{\cdot}00290$.

ii When the concentration of sodium hydroxide is
0·01024 : $\varkappa_m = 0{\cdot}00158$.

From equation (6), we get

i $$C_a = \frac{0{\cdot}00290 - 0{\cdot}008570}{-0{\cdot}154} = 0{\cdot}00368,$$

ii $$C_a = \frac{0{\cdot}00159 - 0{\cdot}004363}{-0{\cdot}154} = 0{\cdot}00180.$$

Therefore the concentrations of free alkali and phenol are altogether

i $0{\cdot}03877 - 0{\cdot}00368 = 0{\cdot}00020$,
ii $0{\cdot}01924 - 0{\cdot}00180 = 0{\cdot}000124$.

Then the constant of the hydrolytic dissociation is

i $$\frac{(0{\cdot}00020)^2}{0{\cdot}00368} = 1{\cdot}06 \times 10^{-4},$$

ii $$\frac{(0{\cdot}000124)^2}{0{\cdot}00180} = 0{\cdot}85 \times 10^{-4}.$$

The degrees of the hydrolysis of sodium phenolate at 25·0°C. given in literature are as follows :

| Dilution. | Degree of hydrolysis. | |
|---|---|---|
| 32*l* | ca. 6% | Hantzsch[1] |
| 10*l* | „ 3% | Walker[2] |

From these data the constant of the hydrolytic dissociation is given respectively:

$$K = 1{\cdot}20 \times 10^{-4},$$
$$K = 0{\cdot}93 \times 10^{-4}.$$

## Summary.

(1) The conductivities of the mixture of aniline and hydrochloric acid, and of phenol and sodium hydroxide have been determined, and the empirical formulæ to represent the change of conductivity with concentrations derived.

(2) A method of analysis of a weak base or acid by conductivity measurements has been described.

(3) The constants of the hydrolytic dissociation of aniline hydrochloride and sodium phenolate has been calculated.

1 Ber. D. chem. Ges., **32**, 3084 (1899).

2 Zs. physik. Chem., **32**, 189 (1900).

# On the Equilibrium in the System: Water, Phenol and Benzene.

By

**Shinkichi Horiba.**

(Received July 6, 1914.)

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The partition coefficient of phenol between water and benzene has been already studied by V. Rothmund and N. T. M. Wilsmore[1], but the complete state of the equilibrium of the system consisting of water, phenol and benzene has ever remained undetermined. The present paper gives an account of an investigation to determine the state of the equilibrium of this ternary mixture at 25·0°C.

## Experimental Methods.

For the determination of phenol in a mixture of water and benzene, the usual method with bromine was employed, but for the analysis of the water and benzene in the mixture no chemical method was practicable. When benzene is added drop by drop to an aqueous solution of phenol and strongly shaken, constant turbidity is observed at the saturation point of benzene, and this fact was utilized in the following way. An aqueous solution of a known concentration was put in a long necked flask which was immersed in the thermostat at 25·0°C and strongly shaken by means of an electric motor. Then benzene was added drop by drop from a capillary burette until constant turbidity was observed, and from the volume of benzene added the percentage composition of the saturated solution was calculated. The saturation point of water in benzene solution of phenol was also estimated by a similar method, water instead of benzene being added.

## Results.

For a graphical representation of this ternary system, equilateral triangular co-ordinates were chosen, as usual for such a ternary system,

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1 Zs. physik. Chem., **40**, 611 (1902).

the angular points representing the pure components respectively. Thus the following five saturation curves, as shown in Fig. 1, were obtained:

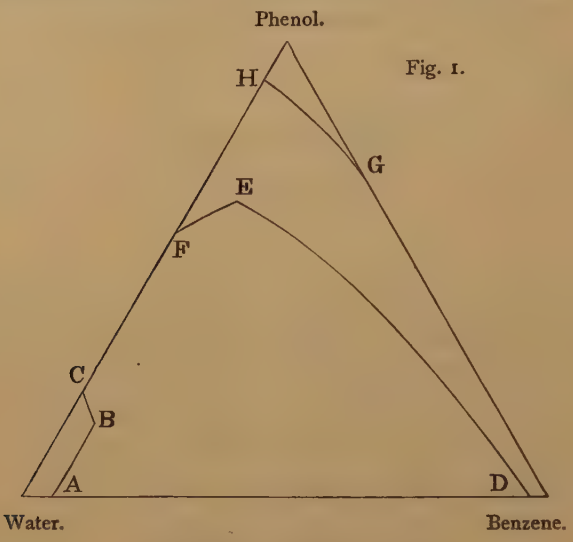



Fig. 1.

(1) The saturation curve of benzene in water (*AB*).
(2) The saturation curve of water iu benzene (*DE*).
(3) The saturation curve of phenol in water (*CB*).
(4) The saturation curve of water in phenol (*FE*).
(5) The saturation curve of phenol in mixture of water and benzene (*HG*).

## Curve 1 and Curve 3.

a) The system: Water and benzene.

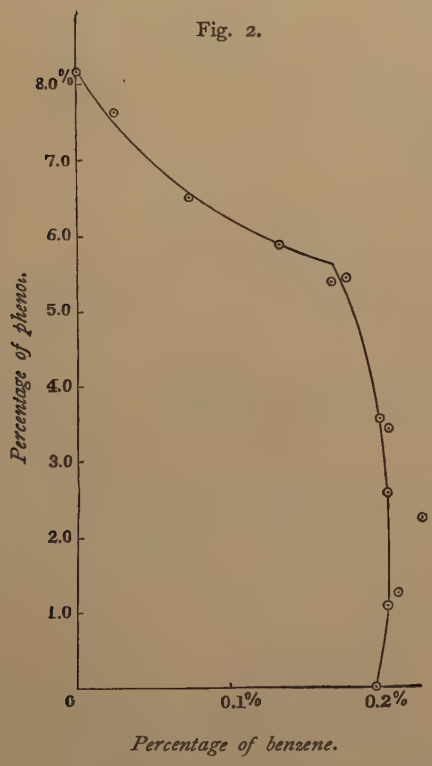
| Water. | Benzene. | Sp. gravity $\left(\frac{25{\cdot}0°C}{25{\cdot}0°C}\right)$. |
|---|---|---|
| 99·802% | 0·198% | 1·0002 |

b) The system: Water, phenol and benzene.

| Water. | Phenol. | Benzene. | Sp. gravity $\left(\frac{25{\cdot}0°C}{25{\cdot}0°C}\right)$. |
|---|---|---|---|
| 98·737 | 1·059 | 0·204 | 1·0008 |
| 98·523 | 1·265 | 0·212 | 1·0010 |
| 97·525 | 2·249 | 0·226 | 1·0020 |
| 97·193 | 2·602 | 0·205 | 1·0021 |
| 96·355 | 3·440 | 0·205 | —— |

| | | | |
|---|---|---|---|
| 96·275 | 3·526 | 0·199 | 1·00305 |
| 94·429 | 5·405 | 0·166 | —— |
| 94·393 | 5·430 | 0·177 | —— |
| 93·915 | 5·953 | 0·132 | —— |
| 93·409 | 6·516 | 0·075 | 1·0059 |
| 92·292 | 7·683 | 0·025 | 100·69 |

Fig. 2.




c) The system: Water and phenol.

| Water. | Phenol. | Sp. gravity $\left(\frac{25{\cdot}0°C}{25{\cdot}0°C}\right)$. |
|---|---|---|
| 99·805 | 8·195 | 1·0073 |

The point *B*, the intersection of the curves *CB* and *AB*, was estimated graphically in Fig. 2, which represents the data for the curves *AB* and *CB* according to rectangular instead of triangular co-ordinates, as follows:

| Water. | Benzene. | Phenol. |
|---|---|---|
| 94·18 | 0·17 | 5·65 |

## Curve 2.

a) The system: Water and benzene.

| Water. | Benzene. | Sp. gravity $\left(\frac{25{\cdot}0°C}{25{\cdot}0°C}\right)$. |
|---|---|---|
| 0·05 | 99·95 | 0·8764 |

b) The system: Water, phenol and benzene.

| Water. | Phenol. | Benzene. | Sp. gravity $\left(\frac{25{\cdot}0°C}{25{\cdot}0°C}\right)$. |
|---|---|---|---|
| 0·24 | 4·78 | 94·98 | 0·8818 |
| 0·81 | 17·36 | 81·83 | 0·9066 |

| | | | |
|---|---|---|---|
| 1·63 | 21·15 | 77·22 | 0·9142 |
| 1·80 | 26·48 | 71·72 | —— |
| 2·18 | 28·01 | 69·81 | 0·9280 |
| 5·05 | 44·39 | 50·56 | 0·9629 |
| 8·07 | 55·80 | 36·13 | 0·9891 |
| 14·49 | 69·18 | 16·33 | 1·0256 |
| 17·72 | 71·46 | 10·82 | 1·0354 |

## Curve 4.

a) The system: Water and phenol.

| Water. | Phenol. |
|---|---|
| 70·71 | 29·29 |

b) The system: Water, phenol and benzene.

| Water. | Phenol. | Benzene. |
|---|---|---|
| 26·75 | 1·62 | 71·63 |
| 23·83 | 2·60 | 73·57 |

The point *E*, the intersection of the curves *DE* and *EF* was estimated in triangular co-ordinates. Its composition was found as follows:

| Water. | Benzene. | Phenol. |
|---|---|---|
| 22·5 | 3·0 | 74·5 |

## Curve 5.

a) The system: Phenol and benzene, with phenol as a residue.

The percentage composition of phenol in the saturated solution in benzene was found as follows:

| | | | |
|---|---|---|---|
| I | 81·02 | II | 81·10 |
| | 80·97 | | 81·10 |
| Mean | 81·03 | | 81·10 |

| Phenol. | Benzene. |
|---|---|
| 81·06 | 18·94 |

b) The system: Phenol, benzene and water, with phenol as a residue.

The percentage compositions of phenol in two different mixtures of water and benzene with phenol as a residue were found as follows:

| Phenol. | Water. | Benzene. |
|---|---|---|
| 92·31 | 3·62 | 4.07 |
| 89·78 | 2·30 | 7·92 |

c) The system: Water and phenol, with a phenol as a residue.

| Phenol. | Water. |
|---|---|
| 95·14 | 4·86 |

## Determination of the Conjugate Points.

The results of the research of the partition of phenol in water and benzene by V. Rothmund and N. T. M. Wilsmore were as follows:

| Phenol in aqueous layer. (Mol. concentration). | Phenol in benzene layer, (Mol. concentration). |
|---|---|
| 0·5299 | 6·487 |
| 0·4853 | 5·735 |
| 0·4523 | 5·040 |
| 0·3688 | 3·046 |
| 0·3660 | 2·978 |
| 0·2847 | 1·512 |
| 0·2578 | 1·254 |
| 0·1816 | 0·638 |
| 0·1013 | 0·279 |
| 0·0532 | 0·129 |
| 0·0272 | 0·062 |

The experimental data for curve 2 were recalculated in molar concentration using the values of specific gravities of those mixtures. Then the composition of the conjugate solutions were estimated graphically by making use of the data of Rothmund and Wilsmore and the percentage compositions of these conjugate solutions were recalculated by help of their specific gravities.

| Upper layer. | | Lower layer. | |
|---|---|---|---|
| Phenol. (Weight percentage.) | Phenol. (Mol. concentration.) | Phenol. (Mol. concentration). | Phenol. (Weight percentage.) |
| 4·78 | 0·4465 | 0·1525 | 1·43 |
| 17·36 | 1·666 | 0·297 | 2·80 |
| 21·15 | 2·047 | 0·320 | 3·01 |
| 28·01 | 2·754 | 0·356 | 3·35 |
| 44·39 | 4·528 | 0·4325 | 4·07 |
| 55·80 | 5·846 | 0·487 | 4·58 |

## The Complete Equilibrium of the System.

| Upper layer. | | | Lower layer. | | |
|---|---|---|---|---|---|
| Phenol. | Benzene. | Water. | Phenol. | Benzene. | Water. |
| 0 | 99·95 | 0·05 | 0 | 0·198 | 99·802 |
| 4·78 | 94·98 | 0·24 | 1·43 | 0·21 | 98·36 |
| 17·36 | 81·83 | 0·81 | 2·80 | 0·21 | 96·99 |
| 21·15 | 77·22 | 1·63 | 3·01 | 0·21 | 96·77 |
| 28·01 | 69·81 | 2·18 | 3·35 | 0·21 | 96·44 |
| 44·39 | 50·56 | 5·08 | 4·07 | 0·19 | 95·74 |
| 55·80 | 36·13 | 8·07 | 4·58 | 0·19 | 95·23 |
| 74·5 | 3·0 | 22·5 | 5·65 | 0·17 | 94·18 |
| 70·71 | 0 | 29·29 | 8·195 | 0 | 91·805 |

## Saturated Solutions

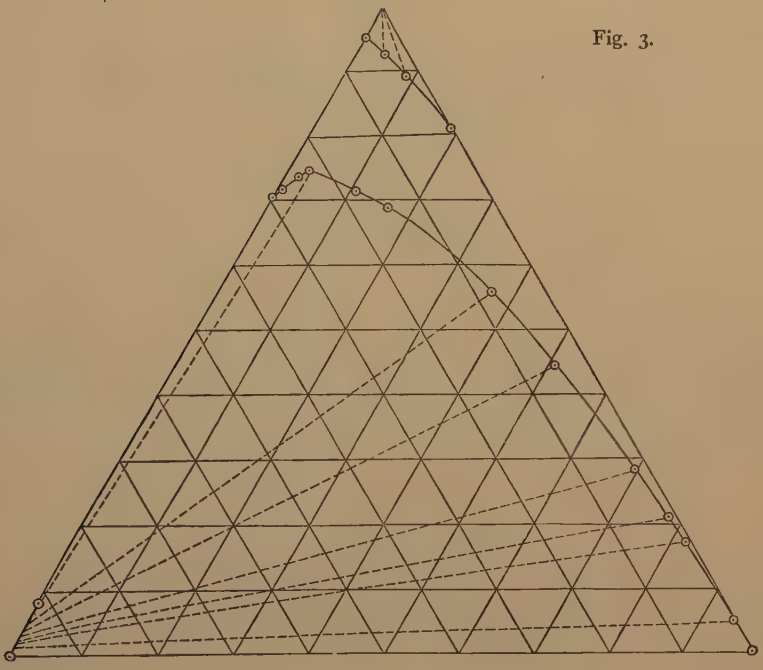
with solid phenol as residue.

| Phenol. | Benzene. | Water. |
|---|---|---|
| 81·06 | 18·94 | 0 |
| 89·78 | 7·92 | 2·30 |
| 92·31 | 4·07 | 3·62 |
| 95·14 | 0 | 4·86 |

The above data are plotted in Fig. 3 which represents completely the equilibrium state of the ternary system in question at 25·0°C.

Phenol.

Fig. 3.



Water. Benzene.

# The System: Lead Oxide—Acetic Acid—Water.

By

**Shigehisa Sakabe.**

(Received July 6, 1914.)

Many basic lead acetates have been described in literature; but in most cases it is doubtful whether they are single compounds. According to Löwe[1] there exist only two basic salts, namely:

$$(C_2H_3O_2)(HO)Pb \text{ and } (C_2H_3O_2)Pb.2(HO)_2Pb,$$

the others being merely mixtures of these basic salts or of one of them and the neutral salt. So far as I know, there has been no systematic study of these compounds in modern times; and I have undertaken to investigate them from the point of view of heterogeneous equilibrium and to verify the conclusion of Löwe.

The materials used were as follows: Commercial pure lead oxide, fused in a platinum crucible to decompose such carbonate as might be contained in it, and used in a finely powdered state; acetic acid of the purest preparation of C. Merck, found to be pure enough for the purpose; and ordinary distilled water, freed from carbonic acid.

The experiments consisted of three series. In the first series of experiments, neutral lead acetate was dissolved in water and lead oxide was added to it, gradually increasing its quantity until the residue contained some lead oxide together with a basic salt. In the second series of experiments, some lead oxide was put in water and acetic acid was added to it in gradually increasing quantities until the residue contained only the basic salt and no oxide. In the third series of experiments, acetic acid was added to an aqueous solution of the neutral salt, the former being used in gradually increasing quantities.

Each experiment was carried out in the following way. The mixture was put in an Erlenmeyer flask of a capacity of about 50 cc., which was made to rotate in a thermostat at 25·0°. The thermometer

1 J. prak. Chem., **98**, 385 (1866).

used was compared with one with a certificate of Physikalisch-Tech nisches Reichsanstalt in Charlottenburg. In cases of acid solutions the equilibrium was attained in a short time, but in cases of basic salts two or three days were required. When the equilibrium was attained, the flask was allowed to stand still in the same thermostat until the suspended matter had completely subsided, then about 2 cc. of the mother liquor were taken out by a pipette, through a short glass tube filled with purified cotton and attatched to its lower end, into a tared flask provided with a well-fitted stopper and subjected to analysis.

To prepare the residue for analysis, it was taken out by a small ladle bottomed with linen and put promptly on folded filter paper on a copper spoon with a long vertical handle held in a large test-tube in the same thermostat. Folded filter paper was placed on it and pressed down with a glass rod to remove as much as possible the adhered mother liquor from the residue. Then the residue, thus prepared, was subjected to analysis. When the residue was a basic salt, however, it was very finely divided, passed through linen even when doubled and was found impossible to remove for analysis in the manner above stated. As it was ascertained that a deviation of about 1° in temperature produces no appreciable chang in the state of equilibrium, the residue was made to deposit in a glass tube by means of a centrifugal machine, the temperature of the surrounding air being kept approximately near 25° by means of lamps. The mother liquor was poured off; and the residue, still wet with mother liquor, was subjected to analysis.

For analysis, the mother liquor was diluted to about 30 cc., and the residue was dissolved in water and, if insoluble in it, with the addition of a known quantity of acetic acid. The lead in the solution was precipitated as lead sulphate by the addition of a given quantity of sulphuric acid; and the precipitate was made less soluble by means of some alcohol added. The precipitate was then treated in the usual way. The acetic acid radical was determined in the filtrate, usual precautions necessary in such a case being observed, by titration with a standard solution of caustic potash, using phenolphthalein as indicator.

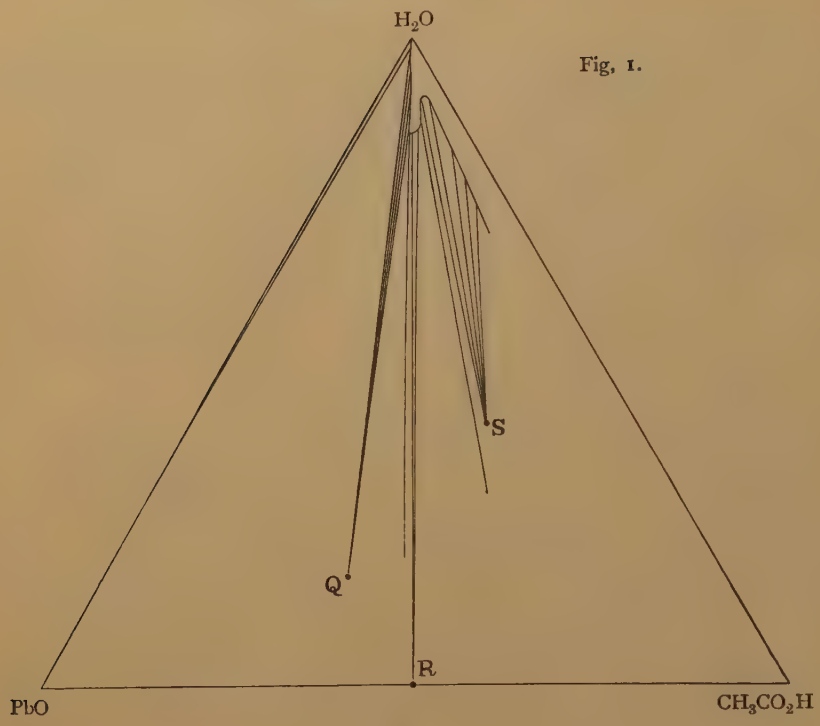
The results of analysis are given in the following table, the components being given in molar percentages:

TABLE I.

| No. | Solution. | | | Residue, wet with some mother liquor. | | | Residue. |
|---|---|---|---|---|---|---|---|
| | Water. | Acetic acid. | Lead oxide. | Water. | Acetic acid. | Lead oxide. | |
| 1 | 98·80 | 0·20 | 1·00 | 79·22 | 0·22 | 20·56 | PbO |
| 2 | 98·45 | 0·48 | 1·07 | — | — | — | „ |
| 3 | 98·41 | 0·54 | 1·05 | — | — | — | „ |
| 4 | 97·52 | 1·03 | 1·45 | 84·09 | 6·21 | 9·70 | $(C_2H_3O_2)_2Pb.2(HO)_2Pb$ |
| 5 | 94·60 | 2·51 | 2·89 | 83·02 | 6·99 | 9·99 | „ |
| 6 | 92·05 | 4·17 | 3·78 | 80·62 | 8·45 | 10·93 | „ |
| 7 | 89·19 | 5·61 | 5·20 | 76·38 | 10·55 | 13·07 | „ |
| 8 | 85·59 | 7·26 | 7·15 | 74·94 | 12·29 | 12·77 | $(C_2H_3O_2)_2Pb.2(HO)_2Pb$ + $(C_2H_3O_2)(HO)Pb$ |
| 9 | 85·70 | 7·79 | 6·51 | 76·42 | 12·26 | 11·32 | $(C_2H_3O_2)(HO)Pb$ |
| 10 | 86·29 | 7·72 | 5·59 | 78·07 | 11·70 | 10·23 | „ |
| 11 | 86·90 | 7·92 | 5·18 | 73·16 | 16·84 | 10·00 | $(C_2H_3O_2)(HO)Pb$ + $(C_2H_3O_2)_2Pb.3H_2O$ |
| 12 | 88·32 | 7·30 | 4·38 | 72·58 | 17·84 | 9·58 | $(C_2H_3O_2)_2Pb.3HO$ |
| 13 | 91·30 | 5·36 | 3·34 | 75·72 | 15·71 | 8·57 | „ |
| 14 | 91·87 | 5·49 | 2·64 | 82·92 | 11·39 | 5·69 | „ |
| 15 | 83·77 | 13·07 | 3·16 | 55·77 | 30·13 | 14·10 | „ |
| 16 | 79·42 | 16·78 | 3·80 | 50·71 | 33·62 | 15·67 | „ |
| 17 | 74·29 | 21·53 | 4·18 | 60·55 | 29·25 | 10·20 | „ |

The chemical compositions of the residues were graphically estimated by referring to triangular coordinates in the usual way, as shown in Fig. 1, and given in the last column of the table. Fig. 2 represents the upper part of the figure on a larger scale to show more clearly the course of the solution curves.

In order to test the existence of any acid salt, the neutral salt was mixed with anhydrous acetic acid; but no acid salt was obtained.




Fig, 1.

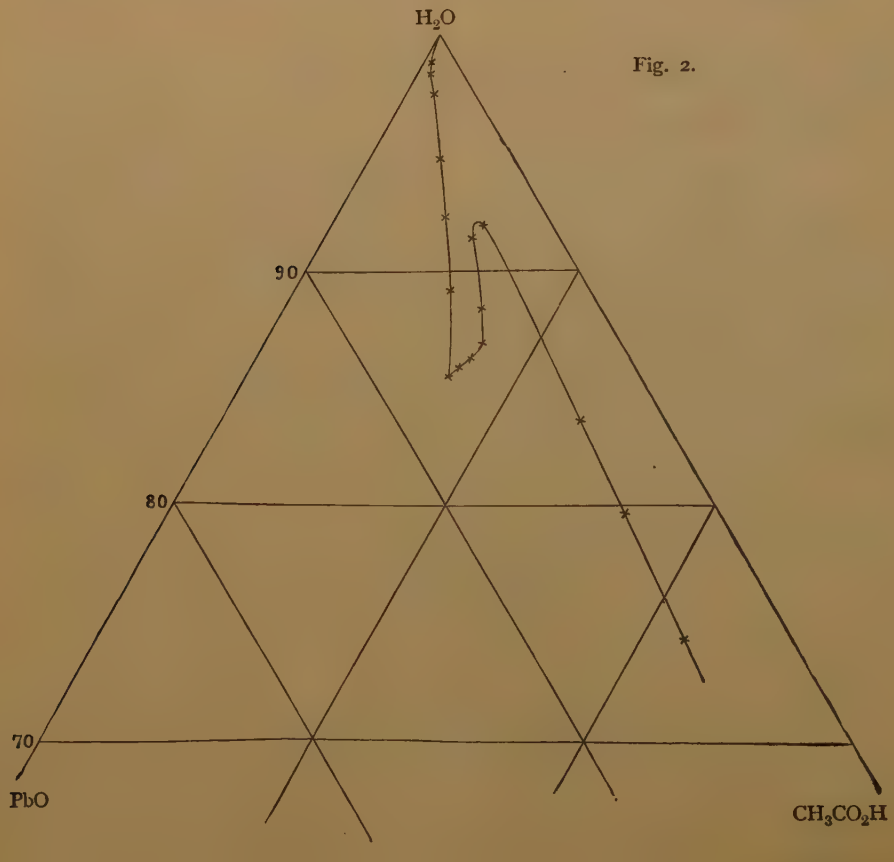



Fig. 2.

## Summary.

1. The two basic lead acetates, $(C_2H_3O_2)(HO)Pb$ and $(C_2H_3O_2)_2Pb.2(HO)_2Pb$, and no other basic salts, have been found to exist in contact with solutions at 25°; and the conclusion of Löwe has been confirmed.
2. No acid salt has been found to exist in contact with solution at 25°.

The author's thanks are due to Prof. Y. Osaka for suggesting the subject of this research and for his interest and advice throughout the work.

# On the Double Salts of Stannous and Potassium Chlorides.

By

**Toshitsune Fujimura.**

(Received July 6, 1914.)

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It is well known that stannous chloride forms several double and complex salts, but the statement in literature concerning those with alkali chlorides are partly conflicting. The comparatively recent investigation of Remsen and Richardson[1] has ascertained, concerning those with potassium chloride, the existence of the following two double salts: $Cl_2Sn.ClK.H_2O$ and $Cl_2Sn.2ClK.2H_2O$. From the stand point of heterogeneous equilibrium a further study of the double salts has been undertaken in order to verify their existence and moreover to determine the conditions for it.

"Extra pure" potassium chloride from C. Merk was recrystallised for use. Stannous chloride ("White Crystal") from the same factory was dissolved in water free from air, granulated tin and hydrochloric acid were added and the mixture was warmed. On cooling the solution gave crystals. Most of the mother liquor was decanted off; and the crystals were placed in a seive funnel in an atmosphere of nitrogen; and the rest of the mother liquor was removed by sucking nitrogen through the funnel and then pressing between folded filter paper. This process was repeated; and the final preparation contained 99·5% salt. Its melting point was 39·5°.

The experiments were begun on one side with water and stannous chloride, and on the other with water and potassium chloride, potassium chloride or stannous chloride, respectively, being added in gradually increasing quantities; and the experiments were carried out in the following way. Some boiled water was added to a mixture of the two salts; and the mixture was heated in a current of nitrogen until a complete

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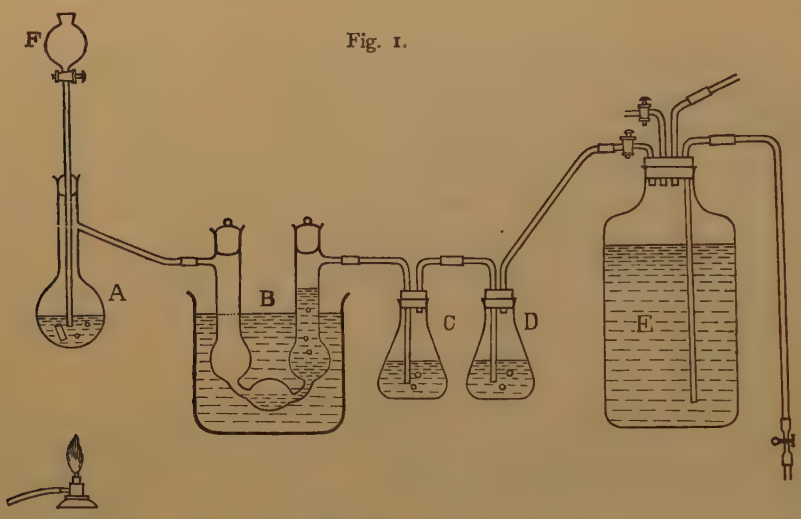
[1] Amer. Chem. J., **14**, 89 (1892).

dissolution took place. The solution was allowed to cool; and in a thermostat at 25·0°C. it was made to rotate for about two hours, as it was ascertained that in that period of time equilibrium would be attained. It was then further allowed to stand in the thermostat; and, when the crystals subsided, a portion of the clear mother liquor was taken out for analysis with a pipette warmed to above 25°C. The residue was taken out with a seive spoon and pressed between folded filter paper in the same thermostat in order to remove as much as possible the adhering mother liquor. The crystals, still wet with mother liquor, were subjected to analysis.

Fig. 1.




The composition of the solution and the wet residue was estimated by determining tin and the total chloride, the former by iodometry in the usual way and the latter by the following somewhat complicated method.

A portion of the sample was weighed in a small glass tube and put into a flask with a side tube and a well fitted glass stopper provided with a funnel as shown in Fig. 1. About 30 cc. of water and some potasssium permanganate in crystals were added. Then the apparatus was set up as seen in the figure; and, while the aspirator *E* was in action, tolerably concentrated sulphuric acid was poured slowly into the flask *A* through the funnel *F*. The mixture of chlorine thus produced and the air entering through *F* passed through the vessels *B* and *C* both of which contained potassium iodide solution. After a period of about one hour *A* was warmed to such a

degree that no oxygen was liberated, and the aspirator was in action still about two hours. During the process *B* and *C* were kept cold to prevent any decomposition of potassium iodide by heat and to make easy the absorption of gas. Then the flask *A* was heated somewhat strongly for about half an hour; and thus after cooling air was again passed through the apparatus for about one hour. Thus the operation ended; and the iodine, liberated by chlorine in *B* and *C*, was titrated by sodium thiosulphate as usual. The flask *D*, which also contained potassium iodide solution, remained always colourless, testifying to the complete absorption of chlorine in *B* and *C*.

To verify the procedure a known mixture of stannous and potassium chlorides was analysed with the following result:

| | Sample taken. | Chlorine in it. | Chlorine found. |
|---|---|---|---|
| Potassium chloride | 0·2730 | 0·1298 | —— |
| Stannous chloride | 0·8827 | 0·1883 | —— |
| Total | 1·1557 | 0·3181 | 0·3168 |

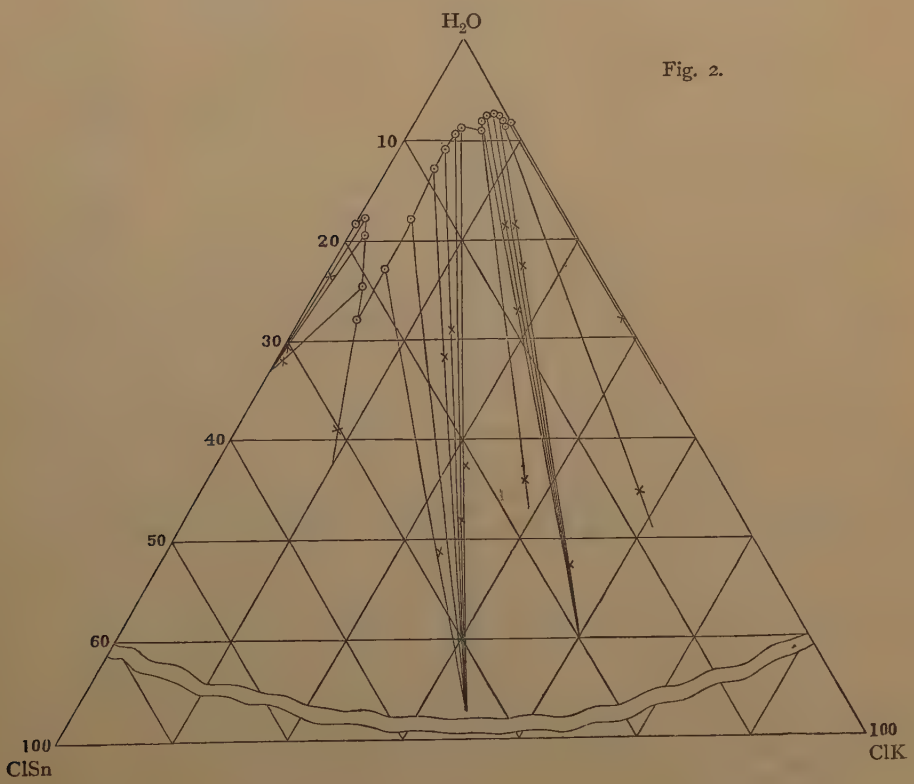



Fig. 2.

From the results of analysis, which was repeated two or three times for the same sample, Table 1 was calculated, while in Fig. 2 these values are represented graphically. In Fig. 2, the three points, to any of which the lines connecting the points representing the solutions and the corresponding wet residues converge, are those representing $Cl_2Sn.2H_2O$, $Cl_2Sn.ClK.H_2O$ and $Cl_2Sn.2ClK.2H_2O$ respectively.

TABLE 1.

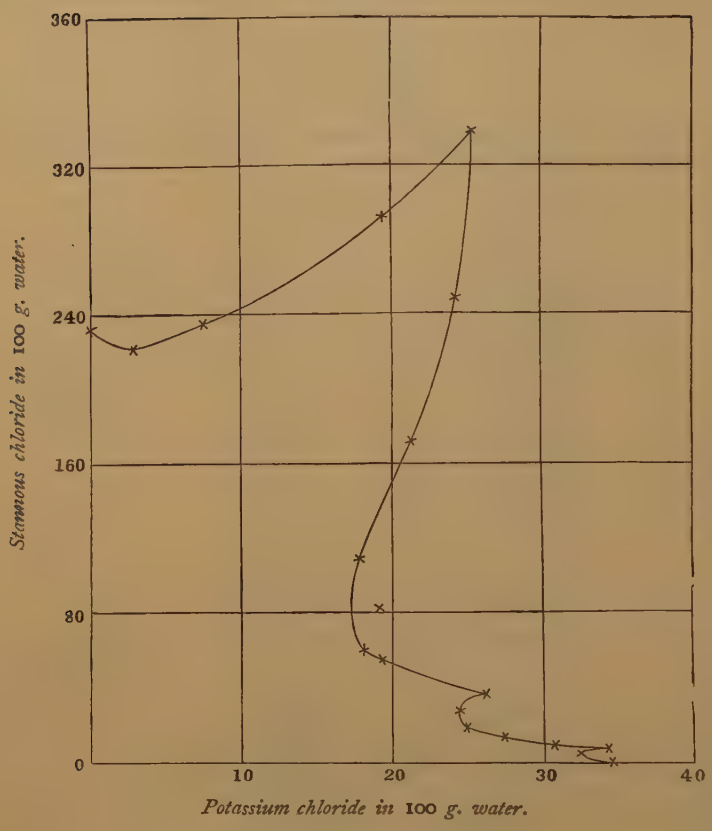
| No. | Solution. (In molar percentage.) | | | Residue wet. (In molar percentage.) | | |
|---|---|---|---|---|---|---|
| | Stannous chloride. | Potassium chloride. | Water. | Stannous chloride. | Potassium chloride. | Water. |
| 1 | 18·17 | — | 81·83 | — | — | — |
| 2 | 17·33 | 0·57 | 82·10 | 23·80 | 0·12 | 76·08 |
| 3 | 18·04 | 1·22 | 80·74 | 30·12 | 0·24 | 69.64 |
| 4 | 20·78 | 3·77 | 75·45 | 31·41 | 0·15 | 68·44 |
| 5 | 23·10 | 4·68 | 72·22 | 30·08 | 8·29 | 62·63 |
| 6 | 18·11 | 4·78 | 77·11 | 27·94 | 23·55 | 48·51 |
| 7 | 13·34 | 4·45 | 82·21 | 14·71 | 6·16 | 79·13 |
| 8 | 8·90 | 3·94 | 87·16 | 17·41 | 14·03 | 88·56 |
| 9 | 6·89 | 4·30 | 88·81 | 15·61 | 13·55 | 70·84 |
| 10 | 5·04 | 4·12 | 90·84 | 24·35 | 23·62 | 52·03 |
| 11 | 4·67 | 4·49 | 90·84 | 20·76 | 21·40 | 57·84 |
| 12 | 2·96 | 6·01 | 91·03 | 16·85 | 27·40 | 55·75 |
| 13 | 2·43 | 5·70 | 91·87 | 8·88 | 18·12 | 73·00 |
| 14 | 1·53 | 5·81 | 92·66 | 5·87 | 12·88 | 81·25 |
| 15 | 0·90 | 6·43 | 92·67 | 6·23 | 15·15 | 78·62 |
| 16 | 0·51 | 7·19 | 92·30 | 4·70 | 13·65 | 81·65 |
| 17 | 0·52 | 7·43 | 92·05 | 16·90 | 35·82 | 47·28 |
| 18 | 0·38 | 7·94 | 91·68 | 7·61 | 38·00 | 54·39 |
| 19 | 0·25 | 7·54 | 92·21 | 0·19 | 27·42 | 72·38 |
| 20 | — | 8·11 | 91·89 | — | — | — |

The compositions of the solution were recalculated in grams solute per 100 grams water and are given in Table 2 and Fig. 3.

TABLE 2.

| No. | Stannous chloride. | Potassium chloride. | Residue. |
|---|---|---|---|
| 1 | 234·05 | —— | |
| 2 | 222·55 | 2·73 | $Cl_2Sn.2H_2O$ |
| 3 | 235·50 | 7·49 | |
| 4 | 290·30 | 19·66 | |
| 5 | 337·20 | 25·51 | |
| 6 | 247·50 | 24·38 | |
| 7 | 170·70 | 21·26 | |
| 8 | 107·65 | 17·79 | $Cl_2Sn.ClK.H_2O$ |
| 9 | 81·78 | 19·06 | |
| 10 | 58·48 | 17·85 | |
| 11 | 54.19 | 19.45 | |
| 12 | 34·28 | 5·99 | |
| 13 | 27·88 | 24·40 | |
| 14 | 17·42 | 24·68 | |
| 15 | 10·24 | 27·30 | $Cl_2Sn.2ClK.2H_2O$ |
| 16 | 5·83 | 30·65 | |
| 17 | 5·95 | 31·76 | |
| 18 | 4·37 | 34·08 | |
| 19 | 2·86 | 32·17 | ClK |
| 20 | —— | 34·73 | |

Fig. 3.




## Summary.

1. The solubility of stannous and potassium chlorides in the presence of each other, at 25°, has been determined.

2. The two kinds of their double salts already known, and no more, have been found to exist at 25°.

3. The conditions under which they can exist at 25° under solutions have been determined.

I desire to express my indebtedness to Prof. Y. Osaka for the suggestion of the subject and advice throughout this investigation.

# Synthesis of Thiohydantoin. III.

By

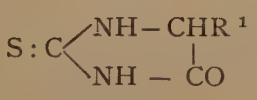
**Shigeru Komatsu.**

(Received July 20, 1914.)

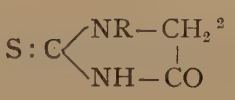
## 1. *Formation of the Substituted Thiohydantoins.*

For the alkyl or aryl derivatives of thiohydantoin the following 4 kinds of structural isomers have already been pointed out to be formed:

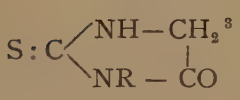
I.



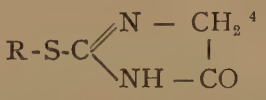
II.



III.



IV.



By the action of thiocyanic acid upon the $\alpha$-amino-acids such as leucine, phenylaminoacetic acid, $\alpha$-aminoisobutyric acid, $\alpha$-aminoisovaleric acid, etc., in presence of acetic anhydride, it has been noticed that there are formed the corresponding acetyl $\alpha$-substituted thiohydantoins which yield respective $\alpha$-substituted thiohydantoins (I) by the action of hydrochloric acid under the separation of the acetyl group.

When $\alpha$-aminoisobutylic acid was used, the yield of the $\alpha$-substituted thiohydantoin was found to be only about 4 percent, which, as the author believe, may be dependent upon the chemical nature of acid. It is also possible that the $\beta$-substituted thiohydantoin corresponding to the formula II, would be formed from thiocyanic acid and sarcosine or phenylglycocolle in the similar manner.

1 Mem. Coll. Sci. Engin, Kyoto, **3**, 11 (1911).

2 Wheeler and Brantlecht, Amer. Chem. J., **45**, 446 (1911).

3 Marckwald, Ber. D. chem. Ges., **24**, 3285 (1891); Aschan, *Ibid.*, **17**, 424 (1884) Brantlecht, J. Biol. Chem., **10**, 139 (1911).

4 Mem. Coll. Sci. Engin. Kyoto, **3**, 9 (1911).

Infering from the analogous behaviours of phenylglycocolle and sarcosine toward urea[1] or phenylthiocyanic acid,[2] it was anticipated that sarcosine may react with thiocyanic acid similarly as phenylglycocolle under the same condition.

When sarcosine and potassium thiocyanate mixed in equimolecular quantities were heated over a water both with acetic anhydride, neither thiohydantoin nor methylamine was found to be formed, sarcosine remaining in solution, as Johnson and Scott[3] have observed in their experiment on phenylglycocolle. When, however, the hydrochloride of sarcosine ethylester prepared by Fischer's method,[4] was heated with potassium thiocyanate in an alcoholic solution, $\beta$-methylthiohydantoin (II.) was obtained just as in the case of phenylglycocolle.[5]

Hence, it is evident that *n*-substituted monobasic $\alpha$-amino-acid has no capability to condense with thiocyanic acid in presence of acetic anhydride, like aspartic and glutamic acids.[6]

Johnson and Guest, having determined the quantities of ammonium chloride formed in the reaction, have to ascribe such a non-formation of thiohydantoin to the deamidation of amino-acids. As amino-acids, however, do not deamidize so easily the author has been led to raise a suspicion with regard to their view. On repeating their experiment precisely following the description, with pure potassium thiocyanate, acetic anhydride and aspartic acid, the following results were obtained:

I. 0·8 grm. ammonium chloride from 2 grms. aspartic acid, 1·5 grms. potassium thiocyanate and 9 c.c. acetic anhydride.

II. 0·75 grm. ammonium chloride from 2 grms. aspartic acid, 1·5 grms. potassium thiocyanate and 9 c.c. acetic anhydride.

III. 1·2 grms. ammonium chloride from 2 grms. aspartic acid, 3 grms. potassium thiocyanate and 1·8 c.c. acetic anhydride.

As seen from the above experimental results, the quantity of ammonium chloride seems to have no relation to that of aspartic acid, but to be dependent upon that of potassium thiocyanate. Hence, it may be concluded that the source of nitrogen recovered in the form

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1 Schwebel, Ber. D. chem. Ges., **10**, 204a (1777); Huppert, *Ibid.*, **6**, 1278 (1873).

2 Wheeler and Brantlecht, Amer. Chem. J., **45**, 446 (1911).

3 J. Amer. Chem. Soc., **35**, 1142 (1913).

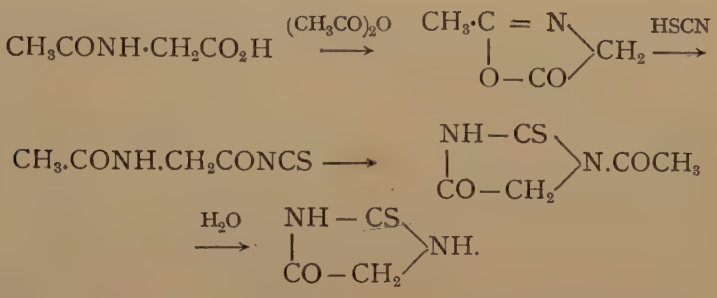
4 Über Aminosäure, Polypeptide u. Proteine, p. 193 (1906).

5 Wheeler and Brantlecht, *Loc. cit.*

6 Amer. Chem. J., **47**, 242; **48**, 160 (1912).

of ammonium chloride would be attributed to potassium thiocyanate but not to aspartic acid.

With regard to the mechanism of the formation of substituted thiohydantoin from monobasic $\alpha$-amino-acid and thiocyanic acid in presence of acetic anhydride, Johnson and Guest[1] have proposed the following scheme for explanation:



Such a view, as above, may apply only to the case of *n*-substituted $\alpha$-amino-acid, but not to the dibasic $\alpha$-amino-acid and pyrrolidon carboxylic acid.

## II. *Mechanism of the Desulphurisation of the Thiohydantoins.*

The thiohydantoins, when heated in neutral or alkaline solution with metallic oxide[2], such as mercury or lead oxide or with potassium permanganate[3], are transformed into the corresponding hydantoins, and also the latter compounds can be prepared by digesting the thio-compounds with chloracetic acid[4] or bromine water[5]. In the case of $\beta$-$\gamma$-disubstituted thiohydantoins desulphurization may be more conveniently effected by the use of 5% nitric acid[6].

Based upon those facts, the author put forward an explanation for the desulphurization of the thiohydantoins upon the assumption that at first addition of a molecule of water may take place under the disruption of a double bond, between carbon and sulphur atoms or

1 *Loc. cit.*

2 Baily and Randolph, Ber. D. chem. Ges., **41**, 2494 (1908); Komatsu, Mem. Coll. Sci. Engin. Kyoto, **3**, 1. (1911).

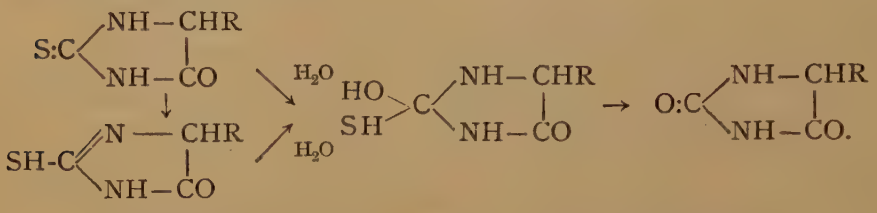
3 H. Biltz, Ber. D. chem. Ges., **42**, 1792 (1909).

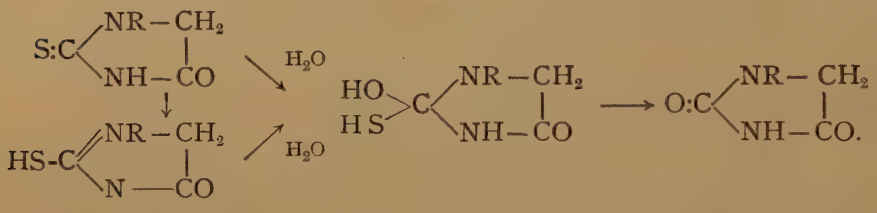
4 Johnson and Guest, Amer. Chem. J., **47**, 245 (1912); Komatsu, Mem. Coll. Sci. Engin. Kyoto, **5**, 13 (1912).

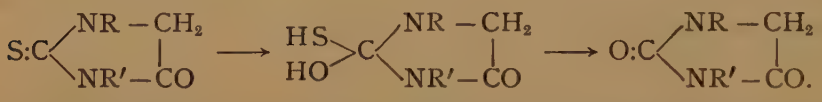
5 Baily and Randolph, *Loc. cit.*

6 Biltz, Ber. D. chem. Ges., **42**, 1792 (1909).

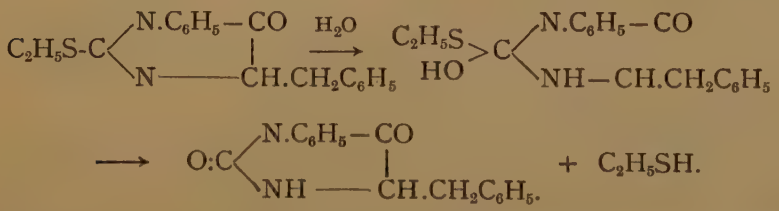
between carbon and nitrogen atoms, and secondarily metallic oxide or other reagents used for desulphurization may simply act to remove hydrogen sulphide from the hydrated compounds, as will be seen in the following representations:



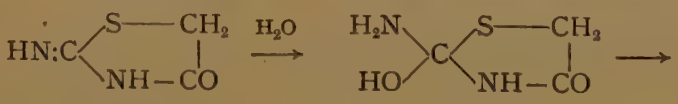




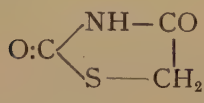
By the similar manner the author has to explain the production of thioalcohol and hydantoin from *s*-alkylthiohydantoin by the action of hydrochloric acid or alcoholic potash[1].

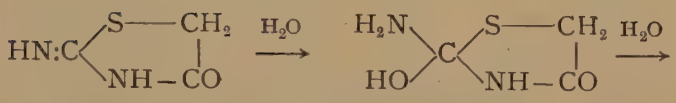


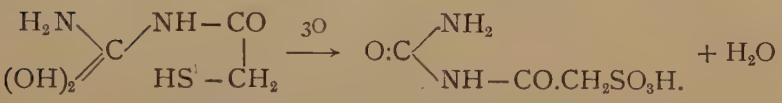
Moreover, the formation of thiocarbamidacetic acid[1] and carbamidosulphoacetic acid[2] from isothiohydantoin, can be explained by the author's view, as will be indicated by the following schemes:



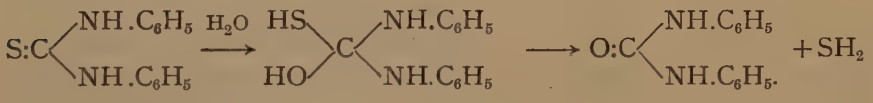
1 Wheeler and Brantlecht, Amer. Chem. J., **45**, 45, 446 (1911); Komatsu, Mem. Coll. Sci. Engin. Kyoto, **3**, 9 (1912).

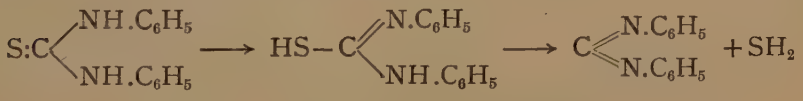






On referring the literatures we find the reactions[3] regarding the transformation of thio-carbanilide to the carbanilide and to carbodiimide, which should be parallel with the author's view of desulphurization. Thus, thiocarbanilide in alcoholic solution, when boiled with mercuric oxide, yields carbanilide, but in the benzene solution carbodiimide; so the author dares to interpret the mechanism of the reactions by the following schemes :

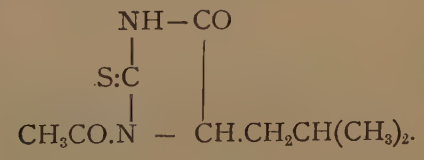




## EXPERIMENTAL PART.

### I. *Condensation of Leucine with Thiocyanic Acid.*

#### 1. *β-Acetyl-α-isobutylthiohydantoin.*



When the equimolecular mixture of potassium thiocyanate and leucine from Merck, was heated with acetic anhydride over a water

1 Volhard, J. prak. Chem., [2]. 9, 6 (1874); May, Lieb. Ann., 168, 133 (1873).

2 Andreasch, Monatsh. Chem., 1, 446 (1880); 6, 131 (1883); Ber. D. chem. Ges., 13, 1423 (1880).

3 Sidgwick, The Organic Chemistry of Nitrogen, p. 191 (1910).

bath for 15 minutes there was obtained a yellow-coloured solution, which on pouring into cold water, deposited the crystals of β-acetyl-α-isobutyl thiohydantoin.

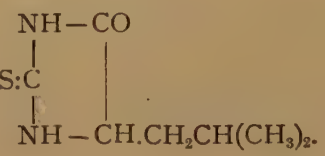
It crystallizes from hot water in colourless scales with silky luster and melts at 112–113°.

The substance is difficulty soluble in cold water, but easily in hot water and alcohol. Its analysis gave the following value for sulphur:

0·1362 grm. substance gave 0·1528 grm. $BaSO_4$.

| | Calc. for $C_9H_{14}O_2N_2S$. | Found. |
|---|---|---|
| Sulphur. | 14·95 | 15·38 |

2. ***α-Isobutylthiohydantoin.***



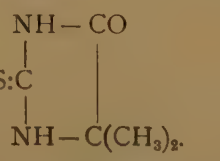
It was prepared by heating acetylisobutylthiohydantoin with conc. hydrochloric acid, and then by evaporating the solution to dryness. The substance was purified by recrystallization from hot water. It crystallizes in colourless scales with silky luster melting at 169–170°. The substance dried over sulphuric acid gave the following value for sulphur by analysis:

0·176 grm. substance gave 0·2352 grm. $BaSO_4$.

| | Calc. for $C_7H_{12}ON_2S$. | Found. |
|---|---|---|
| Sulphur. | 18·60 | 18·31 |

## II. *Condensation of α-Amino isobutyric Acid with Thiocyanic Acid.*

***α-Dimethylthiohydantoin,***



β-Acetyl-α-dimethylthiohydantoin prepared from potassium thiocyanate, α-aminoisobutyric acid and acetic anhydride, as usual, by treating with hydrochloric acid, was converted into α-dimethylthiohydantoin, but its yield was found to be only about 4%.

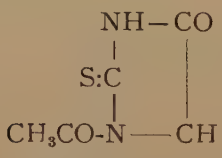
The substance crystallizes in colourless needles, melting at 163–164°.

0·1314 grm. of the substance gave 0·2113 grm. $BaSO_4$.

| | Calc. for $C_5H_8ON_2S$. | Found. |
|---|---|---|
| Sulphur. | 22·22 | 22·26 |

## III. *Condensation of α-Aminoisovaleric Acid with Thiocyanic Acid.*

### 1. *α-**Isopropyl**-β-**acetylthiohydantoin*,

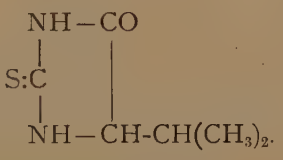


By heating potassium thiocyanate and α-aminoisovaleric acid mixed in molecular proportions with acetic anhydride for an hour, acetylthiohydantoin was obtained in the form of light-yellow oil which by treating with hot water was transformed into a crystalline state. It crystallizes in fine needles from hot water and alcohol, aud melts at 98–99°.

0·1351 grm. of the substance gave 0·1564 grm. $BaSO_4$.

| | Calc. for $C_8H_{12}O_2N_2S$. | Found. |
|---|---|---|
| Sulphur | 16·00 | 15·86 |

### 1. *α-**Isopropylthiohydantoin*,



This compound was prepared by heating acetylthiohydantoin with conc. hydrochloric acid.

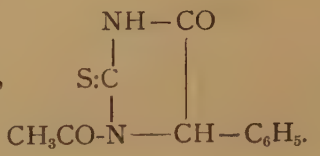
It was purified by recrystallisation from hot water, and crystallizes in colourless plates melting at 129–130°.

0·1717 grm. substance gave 0·2634 grm. $BaSO_4$.

| | Calc. for $C_6H_{10}ON_2S$. | Found. |
|---|---|---|
| Sulphur | 20·30 | 21·00 |

## IV. *Condensation of Phenylaminoacetic Acid with Thiocyanic Acid.*

1. ***α-Phenyl-β-acetylthiohydantoin,***



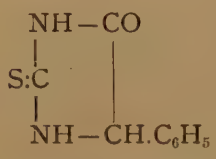
When the reaction product of potassium thiocyanate, phenylaminoacetic acid and acetic anhydride was poured into cold water, a yellow syrupy substance produced was found to solidify on standing.

It crystallizes in colourless needles from hot water, and melts at 185–186°. Its analysis gave the following value for sulphur:

0·1782 grm. substance gave 0·1913 grm. $BaSO_4$.

| | Calc. for $C_{11}H_{10}O_2N_2S$. | Found. |
|---|---|---|
| Sulphur | 13·70 | 14·75 |

2. ***α-Phenylthiohydantoin,***



By treating acetylphenylthiohydantoin with hydrochloric acid, α-phenylthiohydantoin was obtained in colourless needle-shaped crystals which melt at 211–212° with decomposition.

It is difficultly soluble in cold water, but readily in hot water and alcohol.

0·0918 grm. substance gave 0·1150 grm. $BaSO_4$.

| | Calc. for $C_9H_8ON_2S$. | Found. |
|---|---|---|
| Sulphur | 16·60 | 17·20 |

## V. *The Action of Thiocyanic Acid upon Aspartic Acid.*

For this purpose the author repeated Johnson and Guest's experiments exactly following their statement, but has reached the different results. 2 grms aspartic acid from Kahlbaum, 1·5 grms. potassium thiocyanate and 9 c.c. acetic anhydride from Merck were mixed together in an Erlenmeyer flask and heated for half an hour, and 0·8 grm. ammonium chloride was obtained in the first experiment and 0·75 grm. in

the second, instead of 1·3 grms. ammonium chloride which ought to be formed from 2 grms. aspartic acid according to two chemists.

To the reaction product a solution of copper acetate was added, and after a while green crystals were found to separate out. The salt recrystallized from hot water was confirmed to be copper aspartate by analysis.

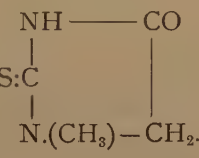
0·2052 grm. substance gave 0·0618 grm. CuO on ignition.

| | Calc. for $C_4H_5O_4NCu4\frac{1}{2}H_2O$. | Found. |
|---|---|---|
| Copper | 23·19 | 24·09 |

This shows that the most part of aspartic acid remains unchanged. In the third experiment, 2 grms. aspartic acid, 3 grms. potassium thiocyanate and 1·8 c.c. acetic anhydride having been used, the author has obtained 1·2 grms. ammonium chloride, corresponding to 75% of its quantity equivalent to nitrogen contained in potassium thiocyanate used. The results of experiments as has been shown, point out that aspartic acid is not the source of ammonium chloride, i.e., that it is not deamidized.

## VI. *The Action of Thiocyanic Acid upon Sarcosine.*

1. ***β-Methylthiohydantoin,***



Hydrochloride of sarcosine ethylester prepared by Fischer's method[1] was heated in a flask together with potassium thiocyanate and alcohol over a water bath for 5 hours, and then alcohol distilled off. On adding cold water to the residue, there separated out orange yellow crystals. The substance was recrystallized several times from hot water, and finally obtained in yellow scaly crystals which melt at 214–215°. It is soluble in hot water and alcohol. The substance dried by heating at 100° for 2 hours gave the following value for sulphur by analysis:

0·121 grm. of the substance gave 0·2222 grm. $BaSO_4$.

| | Calc. for $C_4H_6ON_2S$. | Found. |
|---|---|---|
| Sulphur | 24·62 | 25·12 |

1 *Loc. cit.*

2. Equivalent mixture of sarcosine and potassium thiocyanate was heated with acetic anhydride over a water bath; there was noticed brisk evolution of a gas, with the formation of a brownish yellow solution. The latter was poured into cold water but no separation of methylthiohydantoin was observed; then the solution was distilled. The distillate was found to contain nothing but acetic acid.

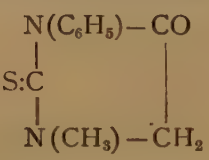
The residue made alkaline with caustic potash was subjected to distillation, and the distillate was found to contain ammonium chloride. Analysis of the platinum double salt gave the following value for platinum.

0·23 grm. platinum double salt gave 0·1006 grm. Pt on ignition.

| | Calc. for $(NH_4Cl)_2PlCl_4$ | Found. |
|---|---|---|
| Platinum | 44·61 | 43·74 |

VII. *Condensation of Phenylthioisocyanate with Sarcosine.*

***β-Methyl-γ-Phenylthiohydantoin,***



The substance was prepared according to Aschan's method from phenylthioisocyanate and sarcosine. It consists of light-yellow platy crystals which melt at 150–151°.

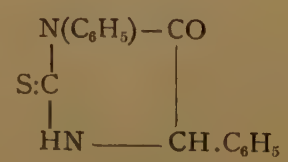
The substance dried by heating at 100° for 2 hours was analysed:

0·1734 grm. substance gave 0·198 grm. $BaSO_4$.

| | Calc. for $C_{10}H_{10}ON_2S$ | Found. |
|---|---|---|
| Sulphur | 15·54 | 15·66 |

VIII. *Condensation of Phenylthioisocyanate with Phenylaminoacetic Acid.*

1. ***α-Phenyl-γ-Phenylthiohydantoin,***



When the equimolecular quantities of phenylthiocyanate and phenylaminoacetic acid in an alcoholic solution was heated with potas-

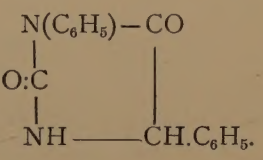
sium hydroxide for 3 hours, the reaction took place, the colour of solution changing orange; then the solution was diluted with water, by which treatment an orange precipitate separated out. The precipitate was washed with cold water, and then treated with hot water. The residue dissolved in hot alcohol deposited reddish brown fine needles which melt at 155–156°. The properties of the compound are now going to be studied by the author, and the results will be communicated in a near future.

A part of the precipitate soluble in hot water crystallizes in fine needles which melt at 223–224°. On analysing the substance dried at 100°, it was confirmed to be $\alpha$-phenyl-$\gamma$-phenylthiohydantoin.

0·235 grm. of the substance gave 0·2021 grm. $BaSO_4$.

| | Calc. for $C_{15}H_{12}ON_2S$. | Found. |
|---|---|---|
| Sulphur | 11·93 | 11·81 |

2. ***α-Phenyl-γ-phenylhydantoin,***



This substance was prepared by boiling $\alpha$-phenyl-$\gamma$-phenylthiohydantoin with chloracetic acid in aqueous solution for 5 hours.

It crystallizes in colourless fine needles which melt at 184–185° (not corrected), while Ehrlich[1] states its melting point to be 191°.

Wondering if the substance may be something else rather than $\alpha$-$\gamma$-diphenylhydantoin, it was analysed:

0·2603 grm. of the silver salt gave 0·087 grm. Ag on ignition.

| | Calc. for $C_{15}H_{11}O_2N_2Ag$. | Found. |
|---|---|---|
| Silver | 30·08 | 29·92 |

1 Biochem. Zs., 8, 453, (1908).

Vol. I., No. 1, Published October 10th, 1914.

*Price - - - yen .60*

These Memoirs are on sale at

MARUZEN COMPANY, LTD.

TOKYO, OSAKA, KYOTO & FUKUOKA.

大正三年十月五日印刷

大正三年十月十日發行

編纂兼發行者　京都帝國大學理科大學

印刷者　野村宗十郎

東京市京橋區築地三丁目十一番地

印刷所　株式會社東京築地活版製造所

東京市京橋區築地二丁目十七番地

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